

✓ VAPOR GROWN CARBON FIBERS FROM
BENZENE PYROLYSIS. EFFECT OF
PROCESS VARIABLES ON THICKENING
AND MECHANICAL PROPERTIES

*A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY*

by
Nayan Jyoti Rathi

to the
DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

March 1996.

2 MAY 1996
CENTRAL LIBRARY
FBI
Doc. No. A. 121489

CHE-1996-M-RAT-V



A121489

CERTIFICATE

It is certified that the work contained in the thesis titled **Vapor Grown Carbon Fibers From Benzene Pyrolysis. Effect Of Process Variables On Thickening And Mechanical Properties** , by *Nayan Jyoti Rath*, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.




Dr. Deepak Kunzru

Professor

Department of Chemical Engg.

IIT Kanpur

March, 1996



ACKNOWLEDGEMENT

It has been distinct privilege to have had the meaning of research and education exemplified to me by my thesis supervisor, **Dr D. Kunzru** I again take the opportunity to thank my guide for his guidance, valuable suggestions and pain-taking efforts in each and every step of my work.

I am indebted to **Dr. Ramesh Chand** for his valuable help in my experimental work. Without him , I could not able to make this type of M.Tech. thesis. I am very thankful to **Mr.K. K. Pant** for providing lively atmosphere in the lab.

I am thankful to **Mr.Paul, Mr.Sharma and Mr.Murerji** for providing lab facility .

I delighted to acknowledge all my friends in or outside the I.I.T.,Kanpur. I really have many unforgettable moments throughout my stay in such a zero pollution , well maintained, beautiful etc. **Indian Institute of technology, Kanpur.**

Finally, the financial support provided by aeronautical Research and Development Board is gratefully acknowledged.

Nayan Jyoti Rathi

CONTENTS

	Page No.
List of Figures	IV
List of Tables	VI
Nomenclature	VII
Abstract	IX
CHAPTER	
1. INTRODUCTION	1
2. LITERATURE SURVEY	5
2.1 Fiber Growth	7
2.1.1 Nucleation	7
2.1.2 Lengthening and Thickening of fibers	8
2.2 Modelling of Fiber Growth	10
2.3 Mechanical Properties	10
3. EXPERIMENTAL APPARATUS AND PROCEDURE	12
3.1 Apparatus	12
3.2 Experimental Procedure	15
4. RESULTS AND DISCUSSION	19
4.1 Preliminary Experiments	22
4.2 Lengthening Stage	28
4.2.1 Effect of Lengthening Time	28
4.2.2 Effect of Lengthening Temperature	28
4.3 Thickening Stage	33
4.3.1 Effect of inlet benzene partial pressure	33
4.3.2 Effect of thickening temperature	35

4.3.3	Effect of gas residence time in the reactor	36
4.3.4	Modelling	38
4.4	Morphology of Carbon Fiber	48
4.5	Mechanical Properties	51
5.	CONCLUSIONS AND RECOMMENDATIONS	60
5.1	Conclusions	60
5.2	Recommendations	60
	APPENDIX I	62
	BIBLIOGRAPHY	63

LIST OF FIGURES

Figure	Page No.
1. Schematic Diagram of Experimental Set-Up.	13
2. Photograph of the Experimental Set-Up.	14
3. Paper and frame method of testing tensile strength and Young's modulus of mono filaments.	18
4. Axial Temperature Profiles in the Growth Furnace.	20
5. Temperature-Time Schedule.	21
6. Comparison of average fiber length on fresh and reused substrates.	23
7. Photograph of Vapor Grown Carbon Fiber with Substrate.	27
8. Effect of lengthening time on fiber length. (Lengthening temperature 1120 °C)	29
9. Effect of lengthening temperature on fiber length. (Lengthening time 2 hr.)	31
10. Variation of fiber diameter with thickening time (Thickening temperature 1090 °C and gas residence time 8.5 s)	34
11. Effect of thickening temperature on fiber diameter. (Lengthening temperature 1090°C and lengthening and thickening time 1 hr.each)	37
12. Effect of gas residence time on fiber diameter. (Lengthening and thickening temperature 1090 °C ; lengthening time 2 hr; thickening time 30 min. and benzene mol % in hydrogen 7.7 %)	39

13. Variation of rate of change of diameter on inlet benzene concentration.	43
14. Variation of rate of change of diameter on gas residence time.	44
15. Arrhenius Plot.	47
16. S.E.Micrograph showing bunch of fibers.	49
17. S.E.Micrograph showing transverse cross-section of carbon fiber.	50
18. S.E.Micrograph showing crenulated surface of carbon fiber.	52
19. S.E.Micrograph showing transverse cross-section of fiber grown at higher temperature.	53
20. Load versus Elongation Plot.	54
21. Variation of Young's modulus on fiber diameter. (Fiber length : 15 mm.)	55
22. Variation of Young's modulus on fiber diameter. (Fiber length : 10 mm.)	56
23. Variation of tensile strength on fiber diameter. (Fiber length : 15 mm.)	57
24. Variation of tensile strength on fiber diameter. (Fiber length : 10 mm.)	58

LIST OF TABLES

Table	Page No.
1. Preliminary runs.	25
2. Effect of lengthening temperature on average fiber length, yield and diameter.	32
3. Variation of dD/dt with τ , P_{BO} and T .	46

NOMENCLATURE

a	: constant, defined in equation (8)
A	: preexponential factor, $\text{m s}^{-1.5} \text{atm}^{0.7}$
b	: constant, defined in equation (8)
C	: chart speed of the load-elongation chart, mm./min
$(\text{C}_3 \text{H}_6)_0$: inlet propylene partial pressure, atm.
C_p	: concentration of carbon precursor, mol / l
D	: average fiber diameter, μm
E	: Young's modulus of elasticity, GPa
E_b	: activation energy of benzene decomposition, kcal/mol
H	: cross-head speed of the load-elongation chart, mm/mi
k, k_d^1	: proportionality constant
k_1, k_d	: rate constant
L	: length of the fiber, mm
\bar{l}	: average fiber length, mm
m	: reaction order with respect to the coke precursor concentration for rate of deposition of pyrolytic carbon
n	: power on the coke precursor concentration
P_{Bo}	: inlet benzene partial pressure, atm
P_{Ho}	: inlet hydrogen partial pressure, atm
r_c	: rate of carbon deposited per unit surface area of the fiber, $\text{gm / cm}^2\text{s}$
R	: gas constant, 1.987 cal/mol
s	: constant, defined in equation (6)
t	: time, s

T : temperature, $^{\circ}\text{C}$

T_1 : temperature, K

Greek Letters

ρ_c : density of pyrolytic carbon deposited , gm/cm^3 .

τ : gas residence time, s

τ^* : critical gas residence time, s

ABSTRACT

Carbon fibers were grown on alumina substrates by vapor phase decomposition of benzene in a tubular reactor. The effect of different process variables affecting lengthening and thickening of carbon fibers has been studied. In the lengthening temperature range (1060-1170 °C), the average fiber length increased till 1140 °C, but increasing the temperature beyond 1140 °C had an adverse effect on the average fiber length. The yield of the fibers also followed a similar trend. At constant temperature, the average fiber length increased with lengthening time and levelled to an asymptotic value.

The thickening of the fibers was affected by the inlet benzene partial pressure, gas residence time and temperature. At otherwise identical conditions, the diameter of the deposited fibers increased with an increase in inlet benzene partial pressure (0.077-0.154 atm.) , temperature (1090-1080 °C) or gas residence time (4.3 -21.3 s). An empirical correlation has been developed relating the rate of change of fiber diameter to these variables.

The variation of tensile strength and Young's modulus was also studied and both these properties decreased with fiber diameter.

CHAPTER 1

INTRODUCTION

Carbon fibers are conventionally produced from polyacrylonitrile, pitch or rayon by spinning and stabilization steps. On the other hand, vapor grown carbon fibers (VGCF) are formed directly by decomposition of hydrocarbon (such as benzene or methane) in a hydrogen atmosphere in the presence of transition metal catalyst. The primary motive for the development of VGCF is to produce a less expensive carbon fiber which still has properties comparable to commercial fibers.

One of the most significant properties of VGCF is their high temperature graphitizability. Unlike pitch and PAN based fibers, these can easily be transformed by heat treatment into highly crystalline graphite. The extent of graphitization is higher than that of any other known fibrous carbon type. The tensile strength of VGCF is comparable to that of commercial carbon fibers and it can be enhanced to as high as 7 GPa by graphitization at about 2800°C. VGCF has desirable thermal and electrical properties. VGCF has higher electrical and thermal conductivities than any other fiber; its resistivity at room temperature is 1000 μ ohm. When heated at 3000°C, the thermal conductivity of the fibers at room temperature is about four times higher than that of copper.

Two main areas of carbon fiber applications are the high technology sector which includes aerospace and nuclear engineering and the general engineering and transportation sector, which includes engineering components such as

bearings, cars, fan blade and automobile bodies. However, the requirement of the two sectors are entirely different. The large scale use of carbon fibers in aircraft and aerospace engineering is governed by maximum performance and fuel efficiency, while the cost factor and production requirements are not critical. The use of carbon fibers in general engineering and surface transportation is dominated by cost constraints, high production rate requirement, and generally less critical performance needs. Due to their short size, VGCF will not be a replacement for the continuous PAN or pitch based fibers. Due to their desirable properties, these fibers are well-suited for applications in composites, heat sinks, electrodes and intercalation host materials (Kato et al., 1992).

Three steps are involved in the production of carbon fibers from vapor phase pyrolysis of hydrocarbons. In the first step, ultra-fine catalyst (generally iron) is sprayed on the substrate. These particles serve as the nuclei for fiber growth. The second step involves the catalytic decomposition of the hydrocarbon on the surface of these small (10-30 nm diameter) metal particles. Under appropriate conditions, the metal surface becomes saturated with carbon and precipitates a hollow carbon tube, or filament, of essentially the same diameter as the catalyst particle (Tibbetts, 1990). The particle continuously decomposes the hydrocarbon to produce an ever lengthening filament of graphite, one end of which is anchored to the growth substrate. The third stage of the growth process i.e. thickening of these filaments to macroscopic dimensions by chemical vapor deposition of carbon, occurs when the hydrocarbon concentration

or the temperature is increased significantly above the optimum values of these parameters during lengthening. During this stage, the catalytic particles become encased with carbon and no further lengthening occurs. Very meagre data is available on the effect of process variables on the growth of VGCF, especially using benzene as a hydrocarbon source. Moreover, even the limited published studies available do not reveal all the details of the process conditions.

In the earlier studies conducted in the department (Jayasanker , 1994) the effect of lengthening temperature , lengthening time and the partial pressure of benzene on the average fiber length and fiber length distribution was investigated. Subsequently, Bansal (1995) studied the effect of sulfur concentration in the feed, reactor configuration, gas residence time and the nature of the substrate on the average fiber length. These studies confirmed that in addition to reactor temperature, lengthening time and benzene concentration, the nature of the substrate was also an important parameter. These earlier studies did not focus on the effect of process parameters in the thickening stage or the mechanical properties of the fibers.

The objective of this studies was to investigate the effect of lengthening temperature, lengthening time and partial pressure of benzene on the average length of the fibers deposited on pure alumina substrates. Another objective was to study the effect of thickening temperature, thickening time and partial pressure of benzene on the average fiber length and diameter. A further objective was to measure the Young's modulus and tensile strength

of the fibers produced at various conditions.

CHAPTER 2

LITERATURE SURVEY

The history of carbon fibers goes back to 1889(Hughes & Chambers, 1889) and the work before 1958 has been reviewed by Hillert and co workers(1958),who grew a wide variety of fibers by decomposing n-heptane in a silica tube at 1000°C .They proposed a mechanism for fiber growth consisting of two steps viz. lengthening and thickening.They proposed that the lengthening step consists of the catalytic decomposition of the hydrocarbon vapor on the catalyst particles and that the fibers stopped growing when the catalyst particles were poisoned by some reaction products formed during pyrolysis. In the thickening step, the chemical vapor deposition of carbon from the vapor phase results in increasing the fiber diameter to macroscopic dimensions. The carbon forming potential of the gas can be increased by either increasing the hydrocarbon concentration or temperature(Endo,1988;Tibbetts,1990).

Most of the studies on VGCF have either used methane or benzene as the feed. In the majority of the reported work, methane has been used as the hydrocarbon source and relatively less data is available on VGCF from benzene decomposition. Baker et al.(1972, 1973) studied the formation of carbon filaments from the decomposition of benzene catalyzed by nickel, iron, cobalt or chromium but the fibers obtained by them were of micrometer size . Koyama (1972) was the first to report fibers of up to 25cm length from thermal pyrolysis of benzene.He obtained a good yield by pyrolysing a mixture of benzene and hydrogen at

about 1100°C. Endo and co-workers (Oberlin et al. ,1976 ; Endo and Komaki,1983) studied the structure of these fibers, the catalyst particles responsible for fiber growth and published some growth procedures.

In the 1980s, development was continued by several groups. Katsuki et al. (1981) studied fiber growth from the decomposition of naphthalene-hydrogen mixtures, whereas Tibbetts's group reported on conditions for fiber growth from pyrolysis of methane or natural gas (Tibbetts and Devour, 1986; Tibbetts, 1983; Tibbetts, 1985). Bennisad and co workers also studied carbon fiber growth from methane. They reported both on conditions of growth(Bennisad et al.,1988a) and for catalyst annealing and melting (Bennisad et al., 1988b). Generally two types of reactor configurations have been employed in the studies on VGCF, viz., substrate method and floating catalyst method. In the substrate method, an inert substrate coated with the catalyst precursor material is used to grow fibers (Endo,1988) whereas in the floating catalyst method,the catalyst precursor is also continuously fed into the reactor with the hydrocarbon feed (Tibbetts, 1990).

In order to examine the possibility of the use of the less expensive Linz-Donawitz converter gas instead of pure hydrogen as the carrier gas,Ishioka et al. (1992a, 1992b, 1992c) have investigated the formation of VGCF from CO- CO₂- H₂ mixtures. Ishioka et al.(1993) found that by properly designing the reactor to suppress disturbances in the flow due to thermal convection, straight VGCF can be produced by the floating catalyst method. Tibbetts (1992) has shown that a greater yield of fibers can be

obtained by a using a linearly increasing temperature sweep instead of isothermal operation. Tibbetts et al. (1993) developed a novel reactor to minimize thermophoretic and convective losses while maximizing nucleation of filamentous carbon. Masuda et al. (1993) obtained longer VGCF at high growth rates by employing liquid pulse injection technique. Recently, Tibbetts et al. (1994) studied the role of sulfur. They concluded that sulfur enhances nucleation by liquifying the catalyst particles.

2.1 Fiber growth

Tibbetts (1990) reported a detailed study on fiber growth. A very limited number of published studies are available on fibers longer than a millimeter. Tibbetts group (Tibbetts et al., 1987; Tibbetts 1992) and Bennisad et al. (1988a, 1988b) have obtained longer fibers from methane pyrolysis but there is no significant information available on production of longer fibers from catalytic pyrolysis of benzene.

As mentioned earlier three steps are involved in the growth of VGCF, viz. nucleation, lengthening and thickening. The published information available on these aspects is summarized below.

2.1.1 Nucleation

The key step for the growth of VGCF is the seeding of the catalyst particles. The initial particles should be very small. A considerable decrease in activity is noted as the particle diameter exceeds 15 nm. Retaining the small particle size during the warm-up phase while avoiding particle coagulation to

an ineffective diameter is very important (Bennisad et al., 1988a). There are different methods for catalyst seeding. Endo and Komaki (1983) used vacuum evaporation in an inert gas to obtain ultra-fine particle of catalyst. Galuszka and Back (1983) employed solutions of ferric nitrate (4×10^{-5} mol/l) as the starting material for the deposition of a thin film of iron oxide on quartz substrate. Tibbetts (1992) and Kato et al. (1992) used inert gases (nitrogen or helium) for decomposition of iron nitrate instead of vacuum. Bennisad et al. (1988a) deposited the catalyst on a flexible support progressively heated up to 1150°C . Jayasanker (1994) heated the substrate at a rate of $6^{\circ}\text{C}/\text{minute}$ under the vacuum of 3×10^{-4} mbar for the nucleation of the iron crystallites. The substrate was maintained at 400°C .

2.1.2 Lengthening and Thickening of Fibers

Tibbetts (1990) reported that finding the optimum conditions for filament lengthening is a difficult process. He used 5cm x 0.6cm rectangular alumina substrates (Tibbetts , 1985) as well as 30 cm long nesting cylinders (Tibbetts and Rodda, 1988) to study fiber growth. Bennisad et al. (1988a, 1988b) produced VGCF by using a mixture of constant composition (30 vol% CH_4 - 70 vol% H_2) and variable temperature up to 1150°C . The fibers were thickened at this temperature for 30 minutes. Endo and co workers used benzene instead of methane as the hydrocarbon source (Oberlin et al., 1976; Endo and Komaki, 1983; Koyama et al., 1972). The vaporized benzene was mixed with hydrogen and passed over the substrate containing the catalyst particles. The substrate was heated to more than 1000°C in about 2 hours.

Lengthening was done at about 1100°C and thickening at 1300°C . The benzene concentration was maintained constant throughout the run. They have reported optimum conditions: hydrogen flow rate; 300-350 cc./min., partial pressure of vaporized benzene; 180 mm Hg and decomposition temperature; $1150 - 1290^{\circ}\text{C}$. Under these conditions, in a furnace having a heating zone of 30 cm, a good yield of fibers (diameter 7-60 μm ;length about 30 cm) were obtained. Kato et al. (1992) reported that without a feed of sulfur source, no carbon fibers were formed in their system. A similar behavior was observed by Katsuki et al. (1981) in their study of fiber growth from naphthalene-hydrogen mixture. This group developed sulfur containing catalysts that grew shorter but more prolific fibers than catalysts containing iron alone. Recently Tibbetts (1994) also showed that adding small amounts of sulfur to the iron vastly increased filament formation. He attributed this to be the liquefaction of iron particle by sulfur. Bansal (1995) varied the thiophene concentration in the feed from 0.05 to 2 vol.% and obtained best fibers at a thiophene concentration of 0.1 vol.% in benzene.

Jayasankar et al.(1994, 1996) studied the effect of lengthening duration and temperature on the average fiber length and fiber length distributions at two different benzene concentration (13.2 and 18.6 mol %). In the temperature range (1283 -1353 K) investigated, the maximum average fiber length increased with an increase in temperature. At constant temperature, the average fiber length initially increased with duration of lengthening and finally reached an asymptotic value.

2.2 Modeling of Fiber Growth

Tibbetts et al. (1983) published a model in which the steady state carbon surface coverage on the filament growing particles was determined by the balance between the surface adsorption rate and the rate of diffusion through the solid particles in the filaments. Tibbetts et al. (1992) modeled the fiber growth obtained by a linearly increasing temperature sweep. They assumed that the fiber lengthening rate is proportional to the square of the methane concentration, and that the catalytic particles are poisoned by hydrocarbon burial. Gupta et al. (1993) have proposed a kinetic scheme to model the lengthening step. This two parameter model assumes that the filaments lengthen by the reaction of a pyrolysis product with the growing chains and that the fiber growth is terminated when the catalyst particle is poisoned by some reactive species in the gas phase. Some models have been proposed to explain the experimentally obtained fiber length distribution. Tibbetts (1958) proposed a semi-empirical model for fiber length distributions encountered in methane pyrolysis. Aravind et al. (1993) extended the mechanistic model proposed earlier (Gupta et al., 1993) and predicted the length distributions of VGCF.

2.3 Mechanical Properties

For VGCF derived from benzene, Koyama (1972) reported the tensile strength to be function of fiber diameter. In the temperature of 1100 - 1250°C, the Young's modulus varied between 179 to 392 GPa and the tensile strength varied from less than 1 GPa for fibers with diameter 70 μm to more than 3 GPa for fiber

diameter less than 5 μm . According to Tibbetts and Beetz (1987), natural gas derived VGCF with average diameter of 7.5 μm have an average modulus of 237 GPa. They showed that the apparent dependence of mechanical properties on fiber diameter was due to the non-uniform carbon deposition rates along the length of the reactor. They also reported mechanical properties to be independent of the precursor, whether benzene or natural gas.

Ishioka (1992) determined the tensile strength and Young's modulus for VGCF prepared from Linz-Donawitz converter gas by the floating catalyst method . The tensile strength decreased with increasing diameter and depended strongly on whether the fibers were straight or crooked. The average tensile strength of straight fibers was 2.05 GPa, while that of crooked fibers was 1.09 GPa. Madronero et al.(1995) studied the effect of hydrogen concentration, nature, and the size of catalyst nuclei and the reactor type on the mechanical properties of VGCF.

From the above literature survey, it is evident that the information available on the production of longer VGCF (>1mm) is very limited. The effect of different process variables on the fiber growth is not understood clearly. Thus a study of the growth process, mechanical properties and morphology involved in the VGCF production from benzene is required.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Apparatus

The experiments were conducted in a tubular flow reactor and a schematic diagram of the experimental set up is shown in Figure 1, whereas a photograph of the experimental apparatus is shown in Figure 2. A tubular reactor is particularly suitable because it allows large gaseous residence times and easy accessibility to the center of the reactor. The reactor used for all the runs was a mullite tube (O.D. 25 mm, I.D. 19 mm and length 600 mm) placed horizontally. The reactor was constructed such that the catalyst loaded substrates, on which the fibers were grown, could be inserted and removed from the reactor under controlled conditions. The reactor was heated by two furnaces. The preheater furnace (210 mm long; maximum temperature 1200 K) and the growth furnace (250 mm long; maximum temperature 1700 K) were connected to temperature programmers so that the rate of heating as well as the final temperature could be independently controlled. The preheater furnace was connected to a P-I programmer and controller with a Type K (chromel-alumel) thermocouple as sensor, whereas the bottom furnace was connected to a P-I-D temperature programmer and controller with a Type S thermocouple.

Provision was also made to measure the temperature inside the reactor tube by inserting a Type S thermocouple (Pt-Pt/Rh) through an outlet connector and a Type K (chromel-alumel) thermocouple through the inlet connector. In the reactor, the substrates (50 mm X 10 mm X 3 mm thick), made from alumina, were

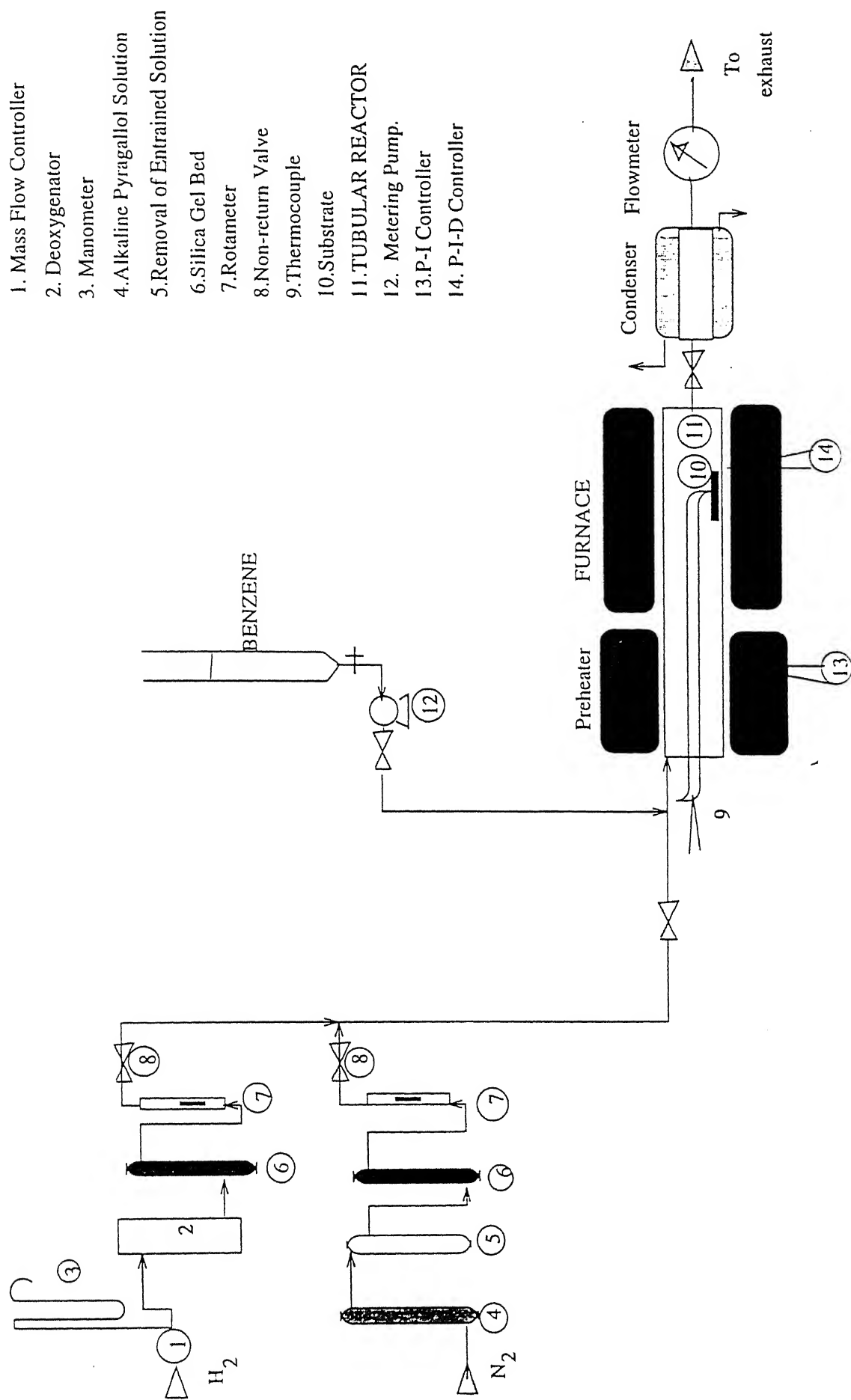


Figure 1 : Schematic Diagram of Experimental Set-Up

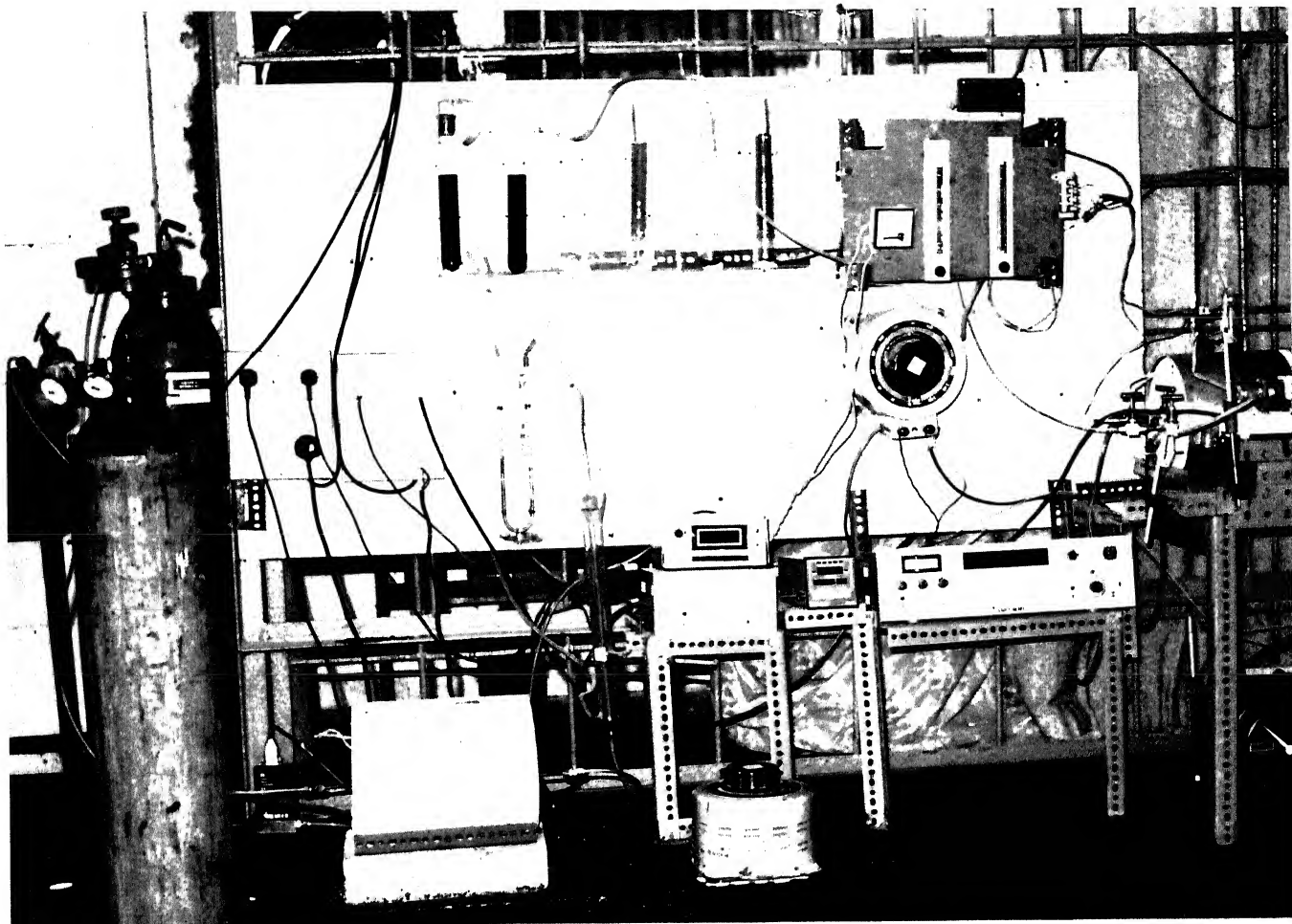


Figure 2 : Photograph of the Experimental Apparatus

used. Extreme care was taken to place the substrate in the isothermal zone of the horizontal reactor.

Benzene (>99% purity) was used as the carbon source. Liquid benzene, containing 0.05 vol % thiophene (99.0 % purity) was pumped into the reactor through a non-return valve. The flow rate of benzene was varied by a metering pump (range :0-0.6ml/min). Nitrogen (99.90% purity) and hydrogen (>99.5% purity) were used as the purging and carrier gases, respectively. Hydrogen was first deoxygenated by passing it through a packed bed containing copper turnings maintained at 773 K and then dried in a silica gel column. The flow rate of hydrogen was controlled using a mass flow controller (range : 0-150 cc/min). The dried, deoxygenated hydrogen was routed to the reactor through a rotameter and a non-return valve. Provision was also made for introducing nitrogen or any other inert gas into the system. This was mainly used for flushing the reactor. Nitrogen was also deoxygenated and dried by passing it through an alkaline pyrogallol solution and silica gel columns, respectively.

The system was operated at atmospheric pressure. The reactor effluent was routed to the condenser . A 10 % glyserol-water solution was used as the coolant in the condenser. Any condensable in the reactor effluent were collected in a liquid collector whereas the noncondensable gases were passed through a gas flow meter and then vented.

3.2 Experimental Procedure

In order to prepare alumina substrates , a weighed quantity (6 g.) of ground alumina powder(S.D.Fine-Chem Ltd., Boisar) was

mixed with a measured volume (2 ml.) of 0.2 % aqueous poly-vinyl alcohol solution. This wet powder was moulded in a die (10 x 1 cm.) and sintered at 1400°C for 8 hours . This substrate was then used for growing fibers. The substrate was coated or sprayed with aqueous 0.1 M ferric nitrate solution. The impregnated substrate was put in the isothermal zone of the growth furnace and heated in a nitrogen atmosphere till 450°C. The substrate was then maintained at 450°C in the nitrogen atmosphere for 10 minutes. After this , the nitrogen flow was stopped and hydrogen was introduced into the reactor, maintained at 450°C. The temperature of the reactor was held constant at 450°C for another 10 minutes. Subsequently, the catalyst particles were reduced by heating the substrate to the lengthening temperature in the hydrogen atmosphere at the rate of 10°C / minute . During this stage, the preheater furnace was also heated at the same rate as the growth furnace but was programmed to remain constant at 750°C . When the growth furnace had reached the lengthening temperature , the flow rate of hydrogen was adjusted to the required value , the temperatures in the two furnaces allowed to stabilize and the feeding of benzene started. Lengthening was continued for a period varying from 15 to 120 min.. Thickening was done either at the same or a higher temperature for 15 to 60 min with the same or different flow rate of benzene and hydrogen , as that used in the lengthening stage. At the completion of thickening, the benzene feed was stopped and the substrate cooled till the temperature in the growth furnace reduced to 800°C.

The VGCF produced were weighed after the completion of the experiment .Fibers grown in the horizontal reactor were easily

scraped from the substrate with the help of a sharp razor and their length measured with the help of a scale . Average lengths were calculated from the fiber length distribution. In order to measure the average diameter of the fibers, the fiber grown substrate was analyzed in an optical microscope (least count: 1 μm) and in a Scanning Electron Microscope (JEOL, Model JSM-840A) In addition, the SEM studies were also used to determine the morphology of carbon fibers.

Testing for mechanical properties was done on a Universal Testing Machine (Instron 1195). The tensile strength and Young's modulus was determined for single filaments by mounting these on a paper frame as shown in Figure 3.

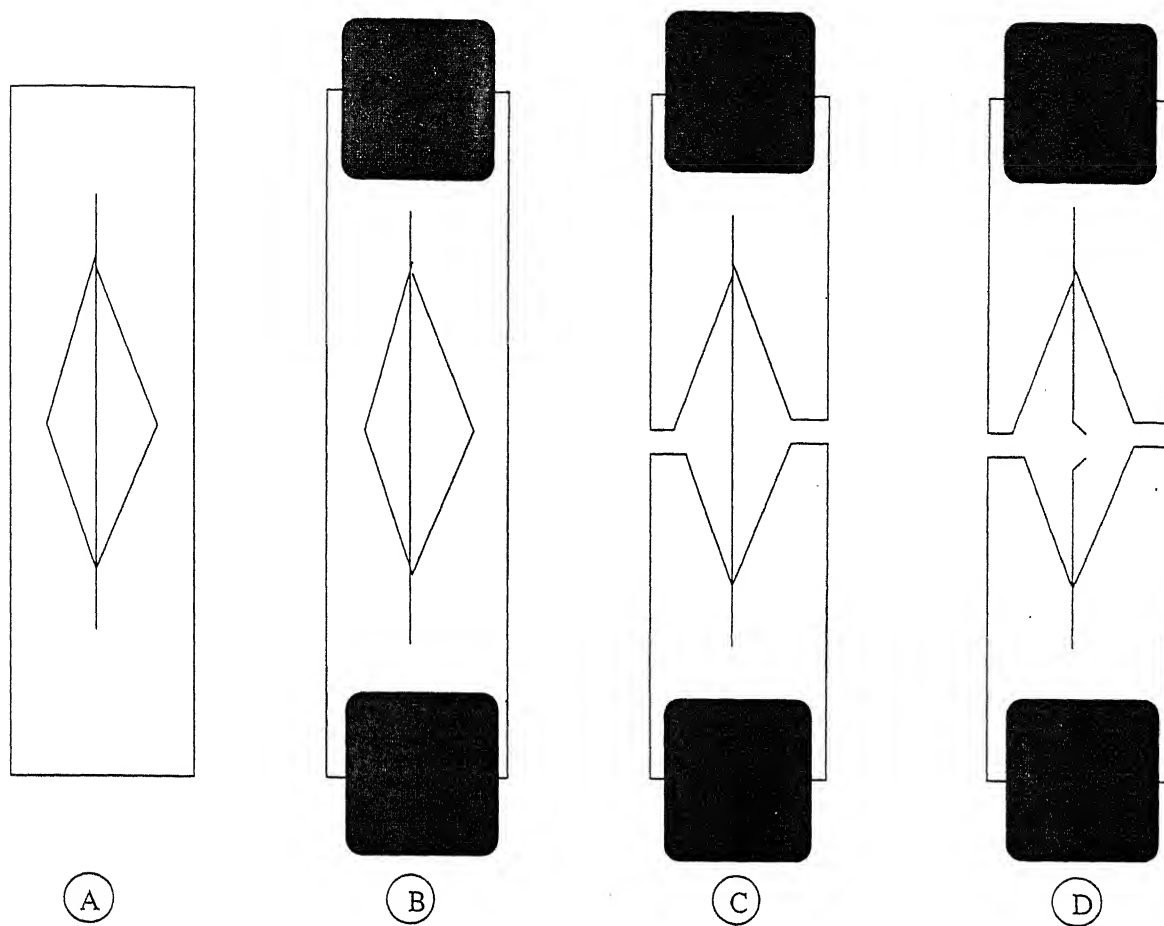


Figure 3 : Paper frame method for testing tensile strength and Young's modulus of mono-filaments.

- A. Paper and frame holding with mono-filament sample fixed by an adhesive on the frame.
- B. The paper and frame holding equipment on the testing machine.
- C. The paper after cutting.
- D. The specimen test sample after measurement.

CHAPTER 4

RESULTS AND DISCUSSION

As mentioned earlier, the benzene pyrolysis experiments were conducted in a horizontal tubular reactor heated by an electric furnace. Due to the entrance and exit losses, the entire reactor could not be operated isothermally. The typical axial temperature profiles of the growth furnace at three different temperature settings are shown in Figure 4. As seen from this figure, the isothermal zone was restricted to approximately 5 cm. Since the aim of the study was to find out the VGCF growth process at isothermal conditions, extreme care was taken to place the 5cm. long substrate in the isothermal zone.

As mentioned in the Section 3.2, after the substrate was positioned in the reactor, the flow of inert gas (nitrogen) and the heating of the reactor was started. The hydrogen was introduced in the system at 450°C and, simultaneously, the inert gas flow stopped. Subsequently, at the desired lengthening temperature, benzene feed was introduced to the system. The typical temperature-time schedule for thickening at 1150°C is shown in Figure 5.

In this study, pure alumina substrates were used. For each experiment, the average length of the carbon fibers (\bar{l}), and the fiber yield was measured. For some experiments, the diameter of fibers was measured by SEM and/or optical microscopy. The reproducibility of the experiments was checked by making repeat runs. Only those experiments for which \bar{l} and yields were reproducible to within $\pm 10\%$ have been reported.

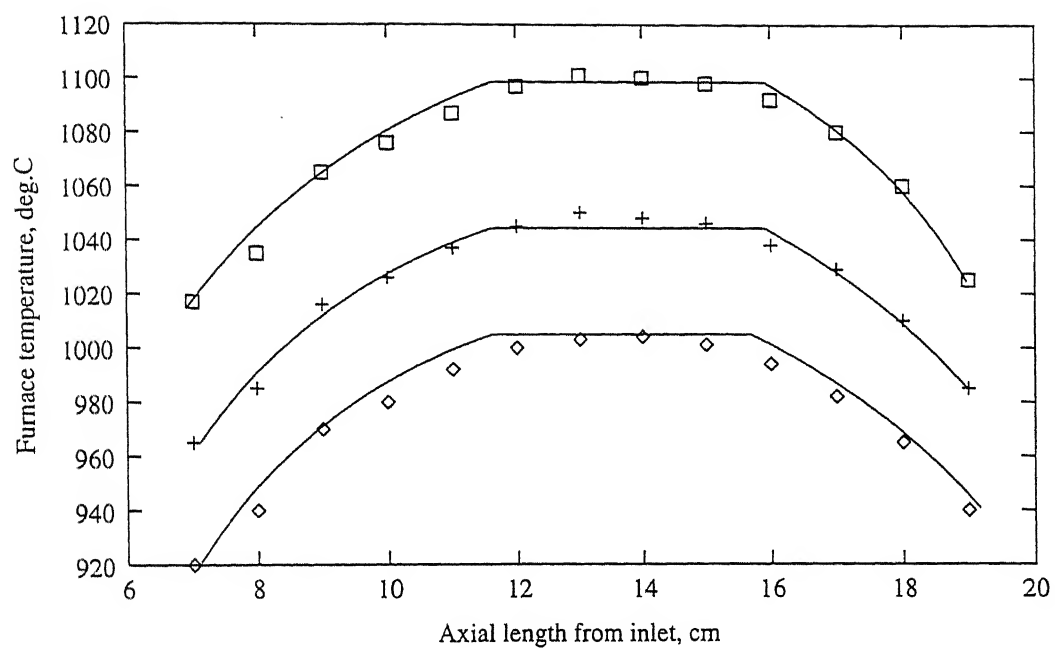


Figure 4 : Axial temperature profiles in the growth furnace

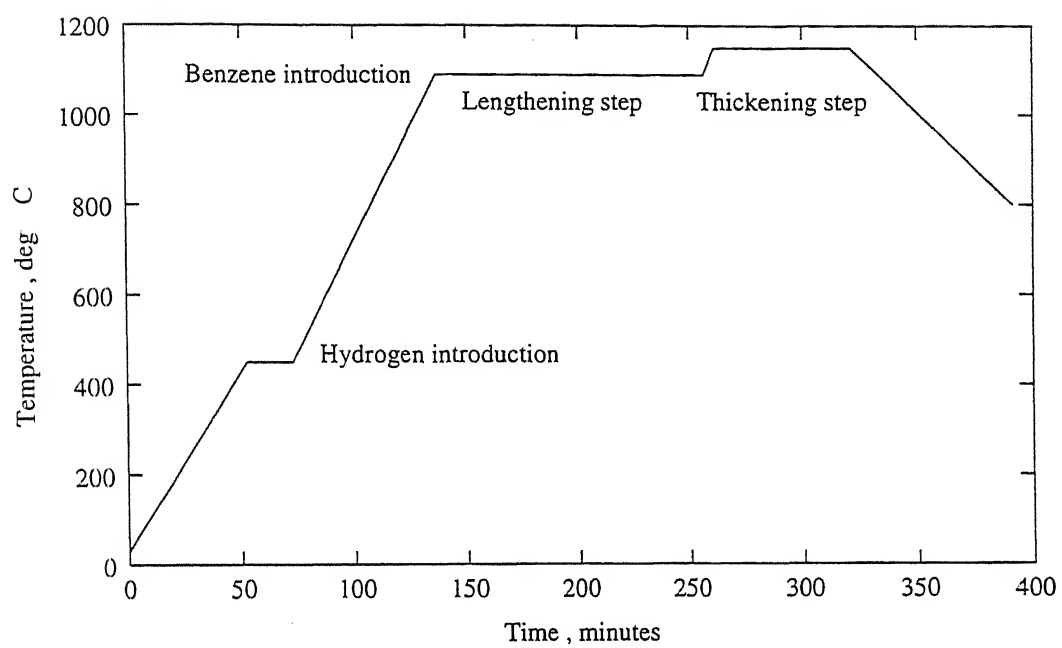


Figure 5 : Temperature -Time Schedule

LIBRARY
I. I. T., KANPUR
Ser. No. A. 121489

4.1 Preliminary Experiments

As mentioned earlier, pure alumina substrates were used for growing the carbon fibers. Preliminary experiments indicated that the fiber yield and \bar{I} were very low when a fresh substrate coated with aqueous ferric nitrate was used. Moreover, the soot formation was also very high. It was noticed that \bar{I} successively increased with repeated use of the substrates. For reusing the substrate, the fibers from the substrates were scraped off after each run, the substrates oxidized at 600°C and then recoated with aqueous ferric nitrate solution. After 6-7 runs of 3 hours duration each, \bar{I} was reproducible. The difference between \bar{I} obtained on a fresh substrate and on a substrate which had been reused for 7 runs, is shown in Figure 6. One reason for the larger \bar{I} on the reused substrates could be the lower porosity of the substrates. The apparent porosity was measured by dipping the substrate in water at room temperature for 5 hours. The apparent porosity was calculated as the difference between the weight of the substrate before and after the dipping divided by the weight of the dry substrate. For the fresh substrate, the porosity was $0.36 \text{ cm}^3/\text{g}$ whereas when the same substrate had been used in 7 runs of 3 hours duration each, the porosity decreased to $0.18 \text{ cm}^3/\text{g}$. Bansal (1995) also found that \bar{I} significantly depended on the substrate porosity. In the case of high porosity substrates, the iron particles may be precipitated inside the pores and thus may not be exposed to the hydrocarbon. Therefore, further runs were conducted only on those substrates which had been earlier used in at least 6 runs.

The growth of VGCF is affected by several process

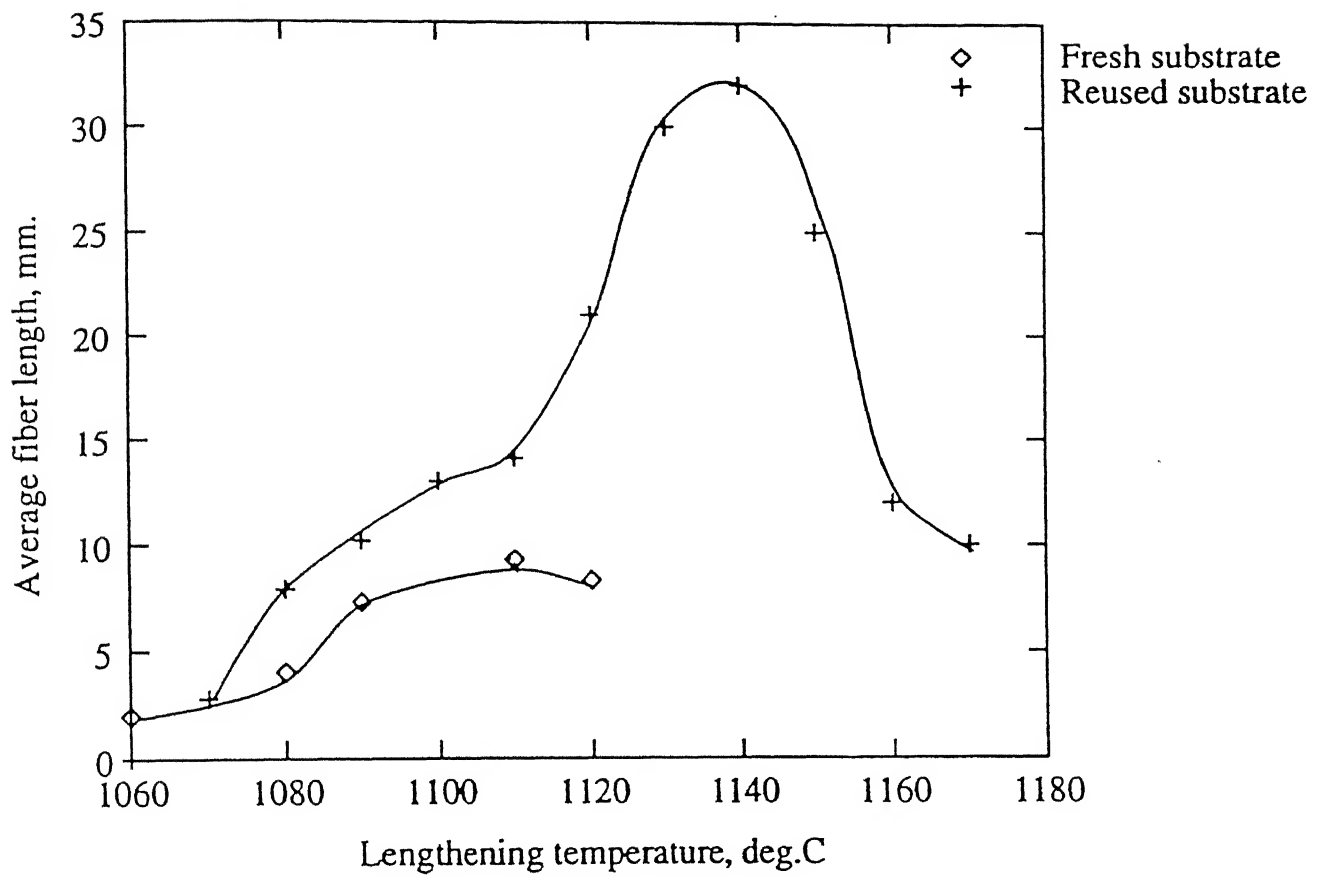


Figure 6 : Comparison of average fiber length on fresh and reused substrates

variables in each of the three steps (i.e. nucleation, lengthening and thickening). In this study, the emphasis was on the lengthening and thickening steps and, therefore, some preliminary runs were conducted to fix the variables which affect the nucleation steps, such as the temperature at which hydrogen was introduced , the ferric nitrate loading on the substrate and the thiophene content of benzene. The effect of these variables on \bar{l} is shown in Table 1. As can be noticed from Table 1, there is an optimum for each of these three variables.

The first step during fiber growth is the nucleation of the catalyst particles, which is obtained by reduction of ferric nitrate. To obtain long fibers, the catalyst particles should be in the range of 12 to 70 nm (Tibbetts, 1985). In addition to the preparation method, the size of the nucleated catalyst depends on the amount as well as the strength of the catalyst precursor solution used to impregnate the substrate. The loading of ferric nitrate on the substrate was varied by varying the volume of the catalyst precursor solution (0.1 M). As can be seen from Runs 1-3 (Table 1), the average fiber length (\bar{l}) was maximum when 0.1 ml of 0.1 M ferric nitrate solution was used for impregnation . This corresponds to an iron concentration of $1.12 \times 10^{-4} \text{ g/cm}^2$ of the substrate.

It is well-known that the size of the iron nuclei depends on the gaseous environment and the temperature maintained during the heating of the substrate (Gadelle, 1990). Hydrogen plays an important role of reducing the catalyst precursor. The sintering of the iron nuclei is also rapid after introduction of hydrogen (Tibbetts, 1992). In order to determine the temperature at which

Table 1 : Preliminary runs

Lengthening temperature = 1070 °C

Lengthening time = 120 minutes

Benzene partial pressure= 0.077 atm.

Run no	Ferric nitrate (0.1 M) loading, ml.	Thiophene content in benzene, vol %	Hydrogen introduction temperature, °C	I mm.
1.	0.05	0.5	450	1.8
2.	0.10	0.5	450	2.8
3.	0.18	0.5	450	nil
4.	0.10	0.5	600	1.0
5.	0.10	0.5	900	0.8
6.	0.10	0.1	450	nil
7.	0.10	0.5	450	2.8
8.	0.10	1.0	450	nil

hydrogen gas should be introduced, runs were conducted in which hydrogen was introduced at three different temperatures (refer Runs 2,4 and 5, Table 1). It is evident from this table, that shorter fibers were obtained when the hydrogen was introduced at a temperature higher than 450°C. This optimum hydrogen introduction temperature is the same as that obtained by Bansal (1995) and Gadelle (1990).

It is well-established that the presence of sulfur in the feed is necessary for good fiber growth (Tibbetts, 1994). In our study thiophene was used as the sulfur source. The effect of sulfur concentration in benzene was investigated by varying the thiophene content of benzene from 0.1-1.0 vol.%. As can be seen from Runs 6-8 in Table 1, \bar{l} of the deposited fibers strongly depends on the sulfur concentration and the best fibers were obtained at a thiophene content of 0.5 vol % in benzene. As reported by Tibbetts et al. (1994), small amount of sulfur reduces the melting point of iron, thereby enhancing filament nucleation.

Thus, for all subsequent runs , hydrogen introduction temperature was kept at 450°C , the iron loading at $1.12 \times 10^{-4} \text{ g/cm}^2$ and thiophene content in benzene at 0.5 vol %. At these conditions, the soot formation was also low and a typical photograph of the as-grown fibers is shown in Figure 7.

In this study, the effect of lengthening temperature and lengthening time during the lengthening stage and the effect of benzene partial pressure, gas residence time and the thickening temperature in the thickening stage have been investigated.

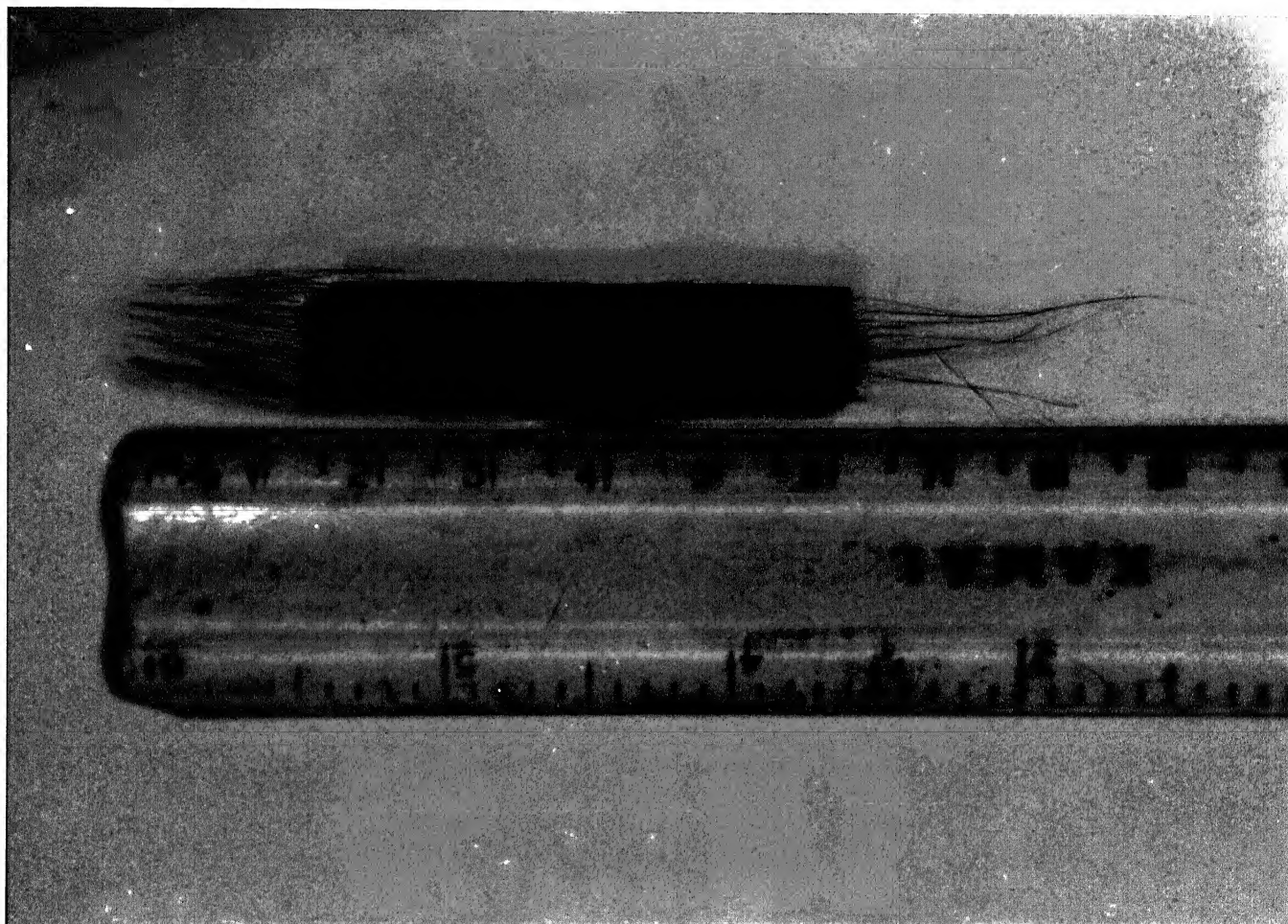


Figure 7 : Photograph of Vapour Grown Carbon fibers with substrate.

4.2 LENGTHENING STAGE

4.2.1 Effect of Lengthening Time

In order to study the effect of lengthening time on the average fiber length of VGCF produced, the duration of lengthening was varied from 15 to 120 minutes. For this set of runs, the hydrogen flow rate was maintained at 30 ml/min, the temperature of the isothermal zone at 1120°C and the benzene concentration in hydrogen at 7.7 mol.%. The thickening time was zero for these runs. As shown in Figure 8, the average fiber length initially increased with lengthening time and then levelled to an asymptotic value. At these conditions, the asymptotic value of \bar{L} was 21 mm. This trend is in agreement with the result reported by Jayasanker et al. (1995) who studied VGCF growth from benzene in the temperature range of $1010-1080^{\circ}\text{C}$. However, the \bar{L} obtained by them was much smaller ($\sim 1-4$ mm). Kato et al. (1981), in their study of growth of VGCF from benzene pyrolysis on the surface of activated carbon pellets, observed an initial induction period of approximately 2 minute followed by a growth similar to that observed in this study. Similar trends of \bar{L} with lengthening time have been reported by Tibbetts (1984) from methane pyrolysis.

As can be noticed from Figure 8, the shape of the plot is sigmoidal but no precise estimate of the induction time could be made because, due to experimental limitation, data for lengthening time less than 15 minutes could not be obtained.

4.2.2 Effect of Lengthening Temperature

The effect of lengthening temperature on \bar{L} was investigated

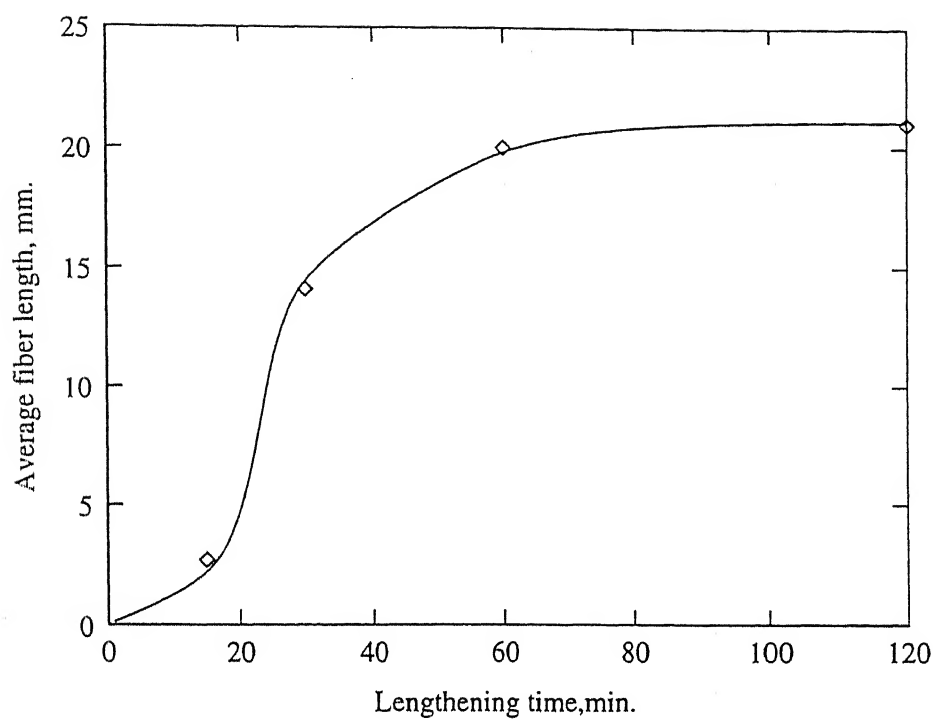


Figure 8 :Effect of lengthening time on fiber length
(Lengthening temperature 1120 deg.C)

in the range of 1040 to 1180°C. For this set of runs, the lengthening time was 2 hr and the benzene concentration in hydrogen was 7.7 mol % . For each run, the average fiber length as well as the fiber yield was determined. The variation of \bar{l} with lengthening temperature is shown in Figure 9 whereas the variation of fiber yield (based on the benzene fed) and average diameter with temperature is shown in Table 2. No fibers were produced below 1060 and above 1170 °C . The fiber production started at 1070°C and the optimum temperature range for fiber growth was 1130-1150°C . In this temperature range, the fiber yields were also highest (Table 2). Except for Run 9 (Table 2), in this temperature range, after 2 hr of lengthening, the average fiber diameter varied between 6 to 20 μm . There was no noticeable trend of diameter with temperature.

Jayasanker et al.(1995) studied the effect of lengthening temperature and inlet benzene concentration on average fiber length. In their study, for inlet benzene concentrations of 13.2 and 18.6 mol % , the average fiber length of the fiber increased with lengthening temperature in the temperature range of 1010 to 1080 °C.

Our result are in good agreement with the results reported by Koyama (1972) and Koyama and Endo (1972) who obtained good yields of VGCF by thermal decomposition of benzene at about 1200°C. For VGCF growth from benzene, Kato et al.(1992) found that \bar{l} was a maximum at 1065°C and decreased at higher temperatures. The optimum lengthening temperature obtained in this study (~1130°C) is significantly higher than at reported by Kato et al.(1992) . The reason for this could be the lower benzene concentration

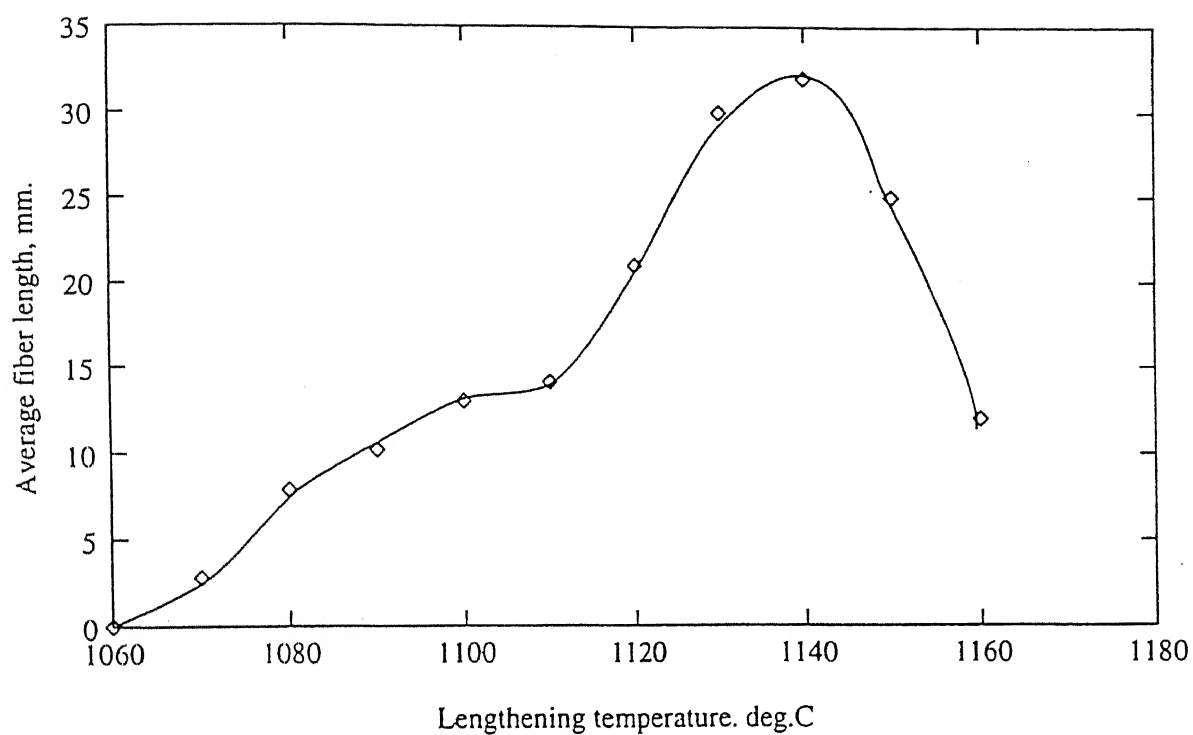


Figure 9 : Variation of average length of carbon fibers with
lengthening temperature
(Lengthening time 2 hr)

Table 2 : Effect of Lengthening Temperature on average fiber length, fiber yield and fiber diameter

S.No	Lengthening temperature, °C	Yield, wt%	Average Length mm	Average Diameter μm
1	1070	< 0.1	2.8	a
2	1080	0.5	7.9	a
3	1090	2.0	10.2	8 ± 2
4	1100	2.3	13.0	a
5	1110	2.3	14.1	a
6	1120	3.3	21.0	17 ± 3
7	1130	8.1	30.0	45 ± 5
8	1140	6.0	32.0	8 ± 2
9	1150	5.8	25.0	11 ± 2
10	1160	0.2	12.0	a
11	1170	< 0.1	10.0	a

a - not measured

(7.7 mol %) compared to 12 mol % in hydrogen used in their study. Tibbetts et al. (1986), in their patent on VGCF production from methane, have reported that the optimum temperature depends on the hydrocarbon partial pressure. For instance, at 1000°C, the optimum methane concentration was 12.5 mol % whereas at 1100°C, the optimum was about 8.0 mol %. Similar temperature ranges (~1100°C) have been employed by Katsuki et al. (1981) for the VGCF formation from naphthalene and by Tibbetts (1986) for VGCF formation from methane.

4.3 THICKENING STAGE

The aim during the thickening step is to deposit pyrolytic carbon on the surface of the fibers. This can be accomplished by either increasing the inlet hydrocarbon partial pressure, the gas residence time or the reactor temperature.

4.3.1 Effect of inlet benzene partial pressure

To study the effect of benzene partial pressure on the thickening stage, the conditions till the end of the lengthening stage were maintained fixed and then the benzene concentration was increased by increasing the benzene flow rate keeping the hydrogen flow rate constant at 30 ml/min. For these runs the lengthening temperature, lengthening time and the inlet benzene concentration during the lengthening stage were 1090°C, 2 hr and 7.7 mol % in hydrogen, respectively. The variation of average fiber diameter with thickening time at three different benzene concentrations is shown in Figure 10. The temperature during the thickening stage was the same as the lengthening temperature.

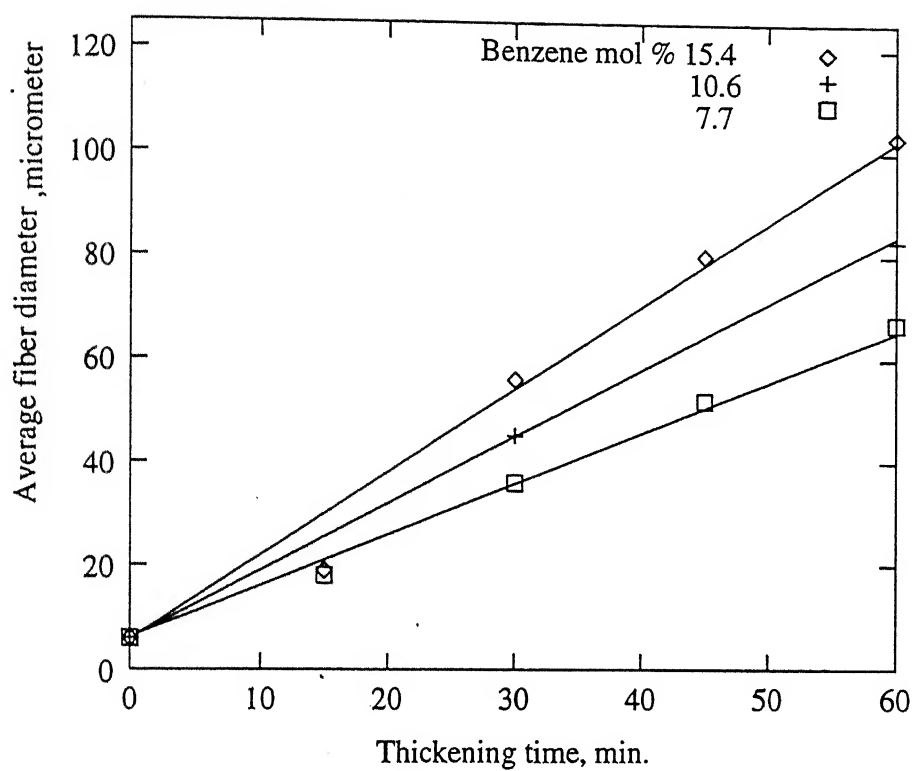


Figure 10 : Variation of diameter with thickening time (Thickening temperature 1090 deg C and gas residence time 8.5 s)

For all the three concentrations studied, the average fiber diameter increased linearly with thickening time. For thickening duration greater than equal to 30 minutes, the average fiber diameter increased with an increase in benzene partial pressure. Kato et al. (1992) in their study VGCF growth using aerosol method also reported that the fiber diameter increased with an increase in the benzene partial pressure.

As can be seen from Figure 10, at a thickening time of 15 minutes, the average fiber diameter obtained for benzene concentration of 7.7 and 15.4 mol% were nearly the same. A possible reason for this could be the finite transit time required for the benzene concentration to increase inside the reactor after the pump setting was increased. The slope of the average diameter versus thickening time plot is proportional to the rate of deposition ($\text{g}/(\text{cm}^2 \text{ of the fiber surface area} \times \text{s})$) of pyrolytic carbon. As can be seen from Figure 10, for each run, the rate of deposition of carbon was constant and did not depend on the fiber diameter. This is in agreement with the results of Tibbetts (1984), who studied the thickening of VGCF using pure methane. In contrast, in the results reported by Gadelle (1990), the rate of deposition decreased with fiber diameter, which was attributed to the mass transfer limitations.

4.3.2 Effect of thickening temperature

To study the effect of temperature on thickening, after the end of the lengthening step, the temperature was increased linearly at the rate of $12^\circ\text{C}/\text{min}$ from the lengthening temperature to the thickening temperature. The temperature during

thickening was varied in the range of 1090-1180 °C . For this set of runs, the lengthening temperature was 1090 °C, the lengthening and thickening time were 1 hr each and the inlet benzene concentration was kept fixed at 7.7 mol % throughout the run . The average fiber diameter obtained after 1 hr of thickening at different temperatures is shown in Figure 11, and as expected, there was a significant effect of temperature on the average fiber diameter. For the same thickening time, the average diameter at 1180 °C was $44 \pm 8 \mu\text{m}$ compared to the average fiber diameter of $8 \pm 4 \mu\text{m}$ obtained at 1090 °C. This is due to the exponential increase in the rate of pyrolytic carbon deposition , as discussed in Section 3.3.4.

No information is available in the published literature on the effect of temperature of the average diameter of the deposited fibers. However, the thickening temperatures used by various investigator are generally in the range of 1100°C. Tibbetts (1990) reported that thickening could be carried out above 1050°C, preferably around 1130°C.

4.3.3 Effect of gas residence time in the reactor

In order to study the effect of residence time on thickening, after the completion of the lengthening step, the flow rates of both benzene and hydrogen were changed such that the benzene concentration was maintained at the same value as used for the lengthening. For these runs, the following conditions were used: lengthening time , 2 hr ; lengthening and thickening temperature 1090°C; benzene concentration in hydrogen, 7.7 mol % ; thickening time , 30 min .

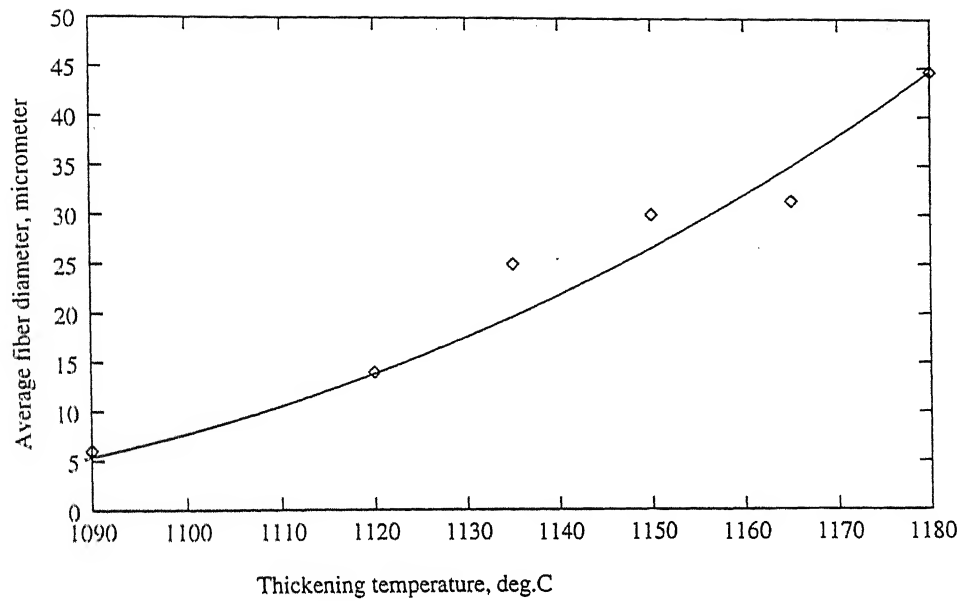


Figure 11 : Effect of thickening temperature on fiber diameter
(Lengthrning temperature 1090 deg.C ; lengthening and
thickening time 1hr. each)

The average residence time (τ) in the heated zone was calculated as the length of the heated zone (5 cm) divided by the linear gas velocity at 1090 °C. The variation of average fiber diameter with average residence time is shown in Figure 12. With an increase in residence time , the concentration of coke precursor increases which results in a higher rate of coke deposition. There is no information available regarding the effect of τ on thickening for VGCF produced by the substrate method. In a related study, Lacava et al. (1982) studied the effect of residence time for the surface carbon formation on copper foil during the pyrolysis of benzene in presence of the hydrogen. The temperature range was maintained at 800-1050 °C. For a fixed temperature , and fixed benzene and hydrogen partial pressures , they reported a critical gas phase residence time below which no significant carbon deposition was measured . Above this critical residence time , the rate of carbon deposition increased linearly with residence time . In this study , a critical residence time was not observed . This is most likely due to the much higher temperatures used in our study.

4.3.4 Modelling

Compared to the nucleation and lengthening stages, the thickening stage is straightforward. It merely consists of the direct chemical vapor deposition of pyrolytic carbon. The rate of change of fiber diameter would depend on the rate of carbon deposition. The rate of carbon deposition, in turn , depends on the concentration of the coke precursors in the gas phase. Due to the complexity of the benzene pyrolysis , no information is available

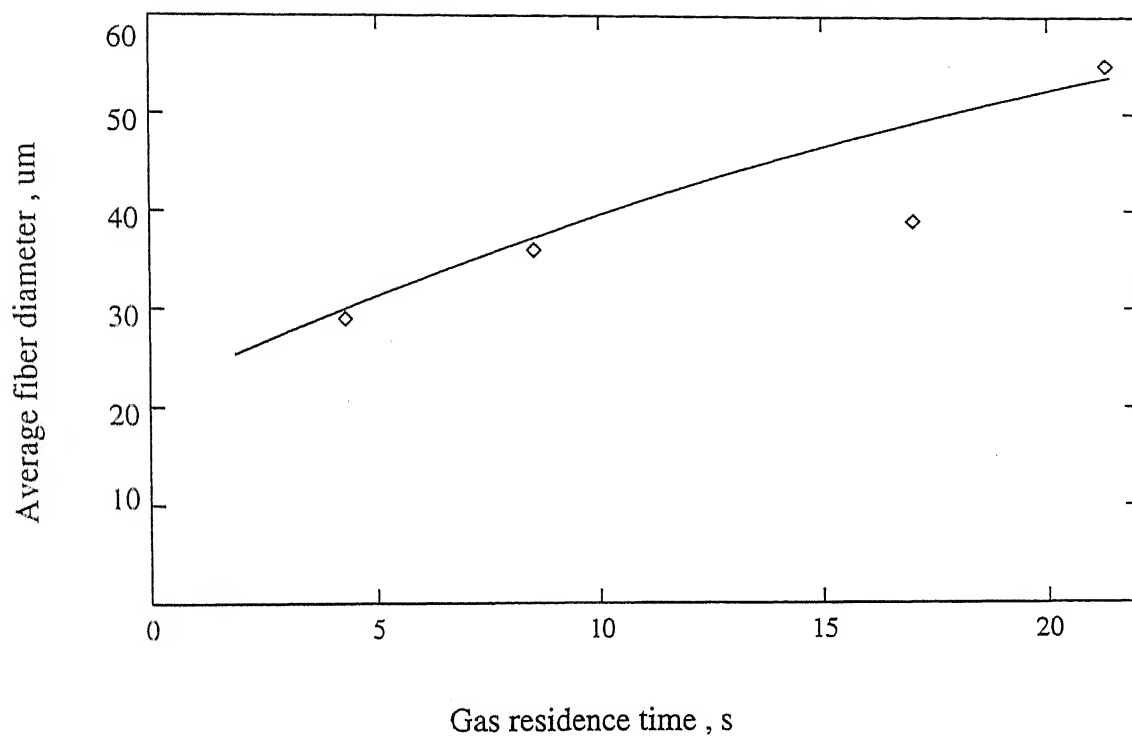


Figure 12 : Effect of gas residence time on average fiber diameter

Lengthening and thickening temperature , 1090°C

Lengthening time , 2 hr

Thickening time , 1 hr

Benzene mol % 7.7

on the exact species which are ultimately dehydrogenated to carbon. Assuming the rate of carbon deposition to be proportional to the surface area of the fibers and to the concentration of the some gas phase carbon precursor, C_p , we have

$$\frac{dm}{dt} \propto (\pi D L) C_p^n$$

or

$$\frac{dm}{dt} = k_d^1 (\pi D L) C_p^n \quad (1)$$

where k_d^1 is a proportionality constant, $\frac{dm}{dt}$ is the mass of carbon deposited on a single fiber, D is the average fiber diameter and L is the length of the fiber.

Then r_c , the rate of carbon deposited in gms/(surface area of fibers x time) can be expressed as

$$r_c = \frac{1}{(\pi D L)} \frac{dm}{dt} = k_d C_p^n \quad (2)$$

As experimentally determined, the average length of the fiber does not vary significantly during the thickening stage. Assuming L to be a constant, we have

$$\frac{dm}{dt} = \rho_c \frac{d}{dt} (\pi D^2 L / 4)$$

or

$$\frac{dm}{dt} = (\rho_c / 2) \pi D L \frac{dD}{dt} \quad (3)$$

where ρ_c is the density of pyrolytic carbon deposited.

Equating (2) and (3), we have

$$\frac{dD}{dt} = (2 / \rho_c) r_c = k_d C_p^n \quad (4)$$

$$\text{where } k_d = 2 k_d^1 / \rho_c$$

In equation (4), k_d is assumed to have an Arrhenius temperature dependency. According to equation (4), for constant temperature and constant coke precursor concentration (C_p), $\frac{dD}{dt}$ would not vary with time, as experimentally observed (Figure 10) .

The concentration of coke precursors , and therefore the rate of carbon deposition, r_c , would depend on the inlet benzene and hydrogen partial pressures. Lacava et al. (1982) have proposed a model for the surface carbon deposition on copper foils from benzene-hydrogen mixtures . The mechanism proposed by them postulates that benzene decomposes to form free radicals; these free radicals then either react with hydrogen to become inactive or react among themselves to form macromolecules . After a critical concentration, these macromolecules condense into droplets. These droplets grow by further addition of macromolecules and collide with the metallic surface and are deposited. Using some simplifying assumptions, they showed that

$$r_c \propto C_p \quad (5)$$

$$\text{where } C_p = k_1 (\tau - \tau^*) P_{Bo} (1 - s P_{Ho}) \quad (6)$$

In equation (6), k_1 is the rate constant for benzene decomposition, τ is the gas residence time, τ^* is the critical gas residence time, P_{Bo} is the initial benzene partial pressure and

P_{H_2O} is initial hydrogen partial pressure and s is constant for a fixed temperature. In their study, s was 0.87 and did not vary significantly with temperature.

Equation (6) was derived assuming that the benzene decomposition was a first order process. For checking the validity of equation (6) to the data of this study, τ^* was taken to be negligible, because experimentally even for the small residence times, appreciable carbon deposited on the fibers. Moreover as reported by Lacava et al. (1982), τ^* decreases with increasing temperature. For their reaction conditions (temperature = 1000°C, $P_{B_0} = 0.132$ atm, $P_{H_2O} = 0.868$ atm.), τ was 5 s. Therefore, for the thickening temperatures used in this work, τ^* would be still lower. Since the partial pressure of hydrogen did not vary appreciably, it was taken to be a constant.

With these assumptions for a given temperature, equation (4) can be written as

$$\frac{dD}{dt} = k_d C_p^n = k_d k_1 \tau P_{B_0} \quad (7)$$

The applicability of equation (7) to the data obtained in this study was checked. A plot of $\frac{dD}{dt}$ versus P_{B_0} at constant τ (8.5 s) and constant thickening temperature (1090°C) is shown in Figure 13, whereas the plot of $\frac{dD}{dt}$ versus τ at constant P_{B_0} and constant temperature is shown in Figure 14. As can be seen from these figures, equation (7) does not satisfactorily represent the experimental data. There is a pronounced curvature in the plots. A possible reason for this lack of fit could be the assumption that

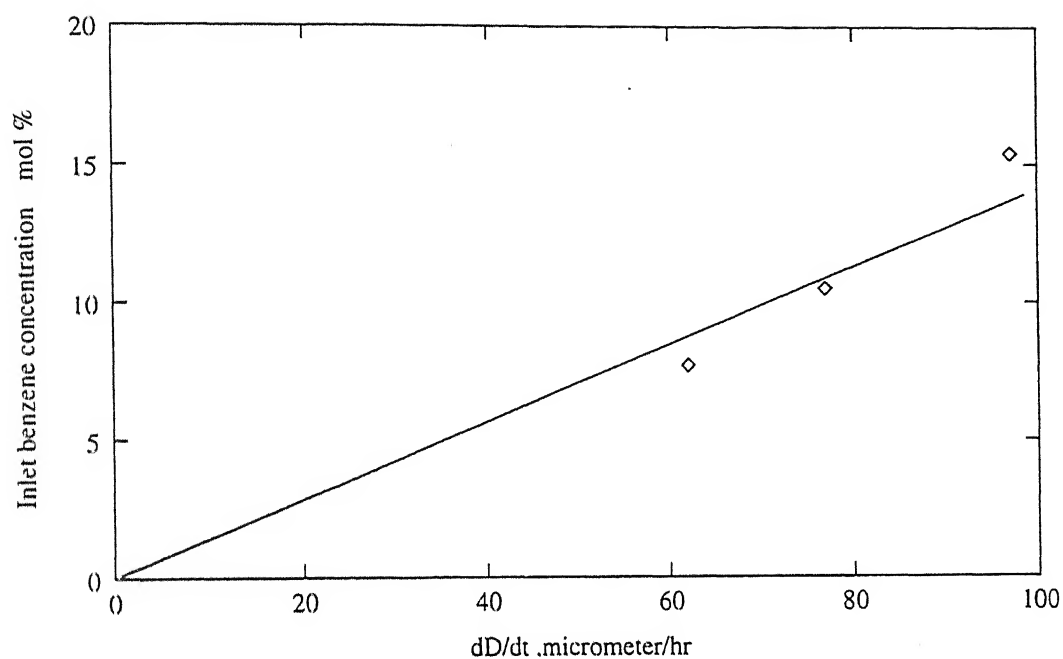


Figure 13 : Variation of rate of change of diameter with
benzene concentration

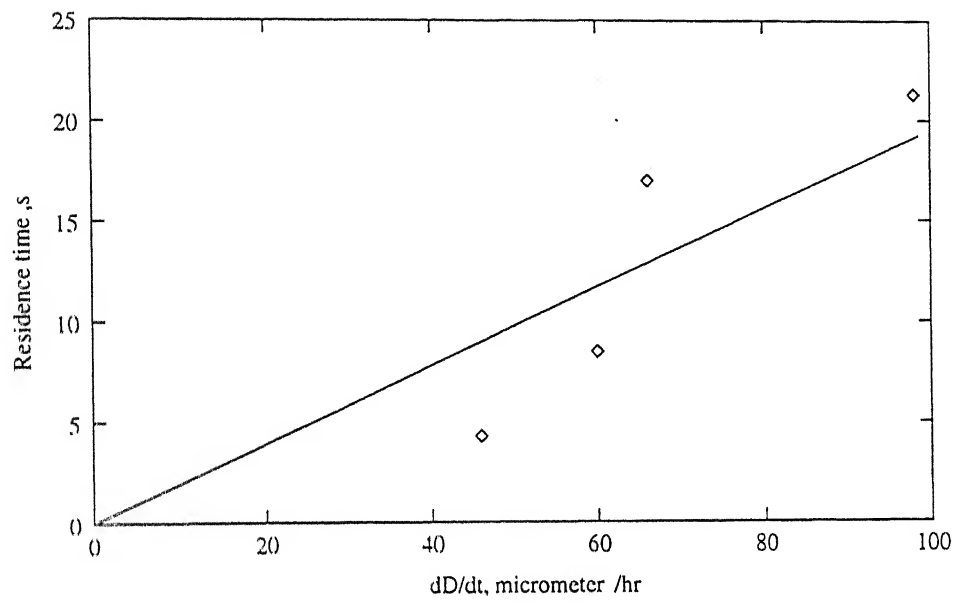


Figure 14 : Variation of rate of change of diameter with gas residence time

the benzene decomposition is a first order process. Although kinetic data for the decomposition of benzene in the presence of hydrogen is not available, the kinetic data available for benzene decomposition indicates that the overall reaction order is between 1 and 2 (Hou and Palmer, 1964).

To obtain the variation of $\frac{dD}{dt}$ with thickening temperature, τ and P_{Bo} , the data was fitted to an empirical expression. The data of $\frac{dD}{dt}$ for all the runs at different T , τ and P_{Bo} are given in Table 3. The empirical expression, used was:

$$\frac{dD}{dt} = A \exp(-E_b / (RT_1)) \tau^a P_{Bo}^b \quad (8)$$

From Run numbers 1 to 4 (Table 3), a was found to be 0.5 whereas from Run numbers 5 to 7 (Table 3), b was calculated to be 0.7. From the data obtained at fixed τ and P_{Bo} and different T (Run number 8 to 13, Table 3) E was calculated from an Arrhenius plot, shown in Figure 15. The activation energy was found to be 107 kcal / mol and pre-exponential factor was $1.7 \times 10^8 \text{ m s}^{-1.5} \text{ atm}^{0.7}$. No information is available on the activation energy of pyrolytic carbon deposition from benzene. However, this value is in good agreement with the activation energy of 87 kcal/ mol reported for pyrolytic carbon deposition from propylene (McAllister et al., 1990). These values of a and b imply that, in the temperature range of 1090 - 1180°C, the concentration of the coke precursor, C_p varies as $\tau^{0.5} P_{Bo}^{0.7}$.

For pyrolytic deposition of carbon from propylene, McAllister et al. (1989) proposed a model for calculating the concentration of the coke precursor. In their model, the allyl radical was

Table 3 : Variation of dD/dt with τ , P_{BO} and T

S.No.	$\frac{dD}{dt}$, $\mu\text{m/h}$	τ , s	P_{BO} , mol %	T , $^{\circ}\text{C}$
1	46	4.3	7.7	1090
2	60	8.5	7.7	1090
3	66	17.0	7.7	1090
4	98	21.3	7.7	1090
5	97	8.5	15.4	1090
6	77	8.5	10.5	1090
7	62	8.5	7.7	1090
8	3	8.5	7.7	1090
9	11	8.5	7.7	1120
10	22	8.5	7.7	1135
11	27	8.5	7.7	1150
12	28	8.5	7.7	1165
13	41	8.5	7.7	1180

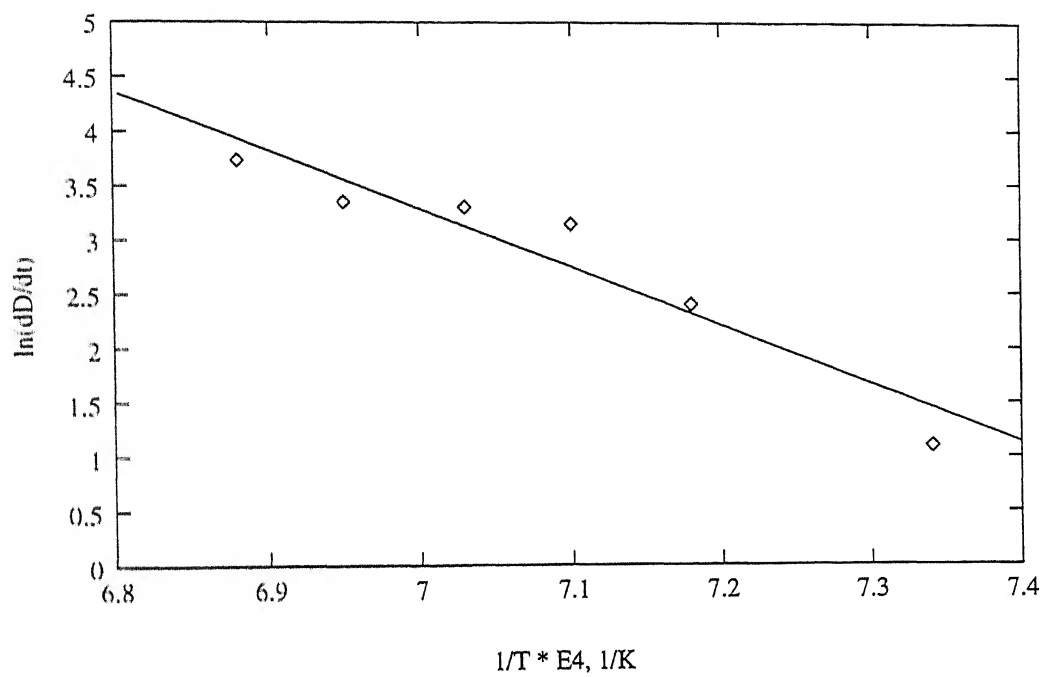


Figure 15 : Arrhenius Plot

proposed to be the radical species which nucleated the carbon precursor. The order of the overall decomposition of propylene was 1.45. Using some simplifying assumptions, the concentration of the coke precursor was expressed as

$$C_p = k (C_3H_6)_0^{0.55} - [0.45 k_1 \tau + (C_3H_6)_0^{-0.45}]^{-1.222} \quad (9)$$

To compare the values of a and b obtained in this study, C_p at a fixed temperature (780°C) and at different values of τ and $(C_3H_6)_0$ were calculated using equation (9) and then fitted to equation (8). For their data, the value of b was 0.6 whereas, the values of a varied between 0.1-0.3, being higher at lower τ .

Thus for both propylene and benzene, the variation of C_p with τ and inlet hydrocarbon partial pressure is similar. This implies that, during VGCF formation from benzene, the coke precursors are formed from reaction intermediates, rather than the reactant.

4.4 MORPHOLOGY OF CARBON FIBERS

Morphology is very important in understanding the properties of VGCF. In this study, the morphology of the as-grown carbon fibers was examined using a Scanning Electron Microscope (SEM).

Figure 16 shows a typical microscope of a bunch of fibers, whereas the transverse cross-section of a single fiber is shown in Figure 17. The cross-section resembles that of a tree with concentric annular rings. These annular rings are formed during the thickening stage by chemical vapor deposition of the carbon on the original filament. The hollow tubular structure of VGCF has been well-documented (Tibbetts, 1990). Some fibers had a crenulated



Figure 16 : S.E. Micrograph showing bunch of fibers.

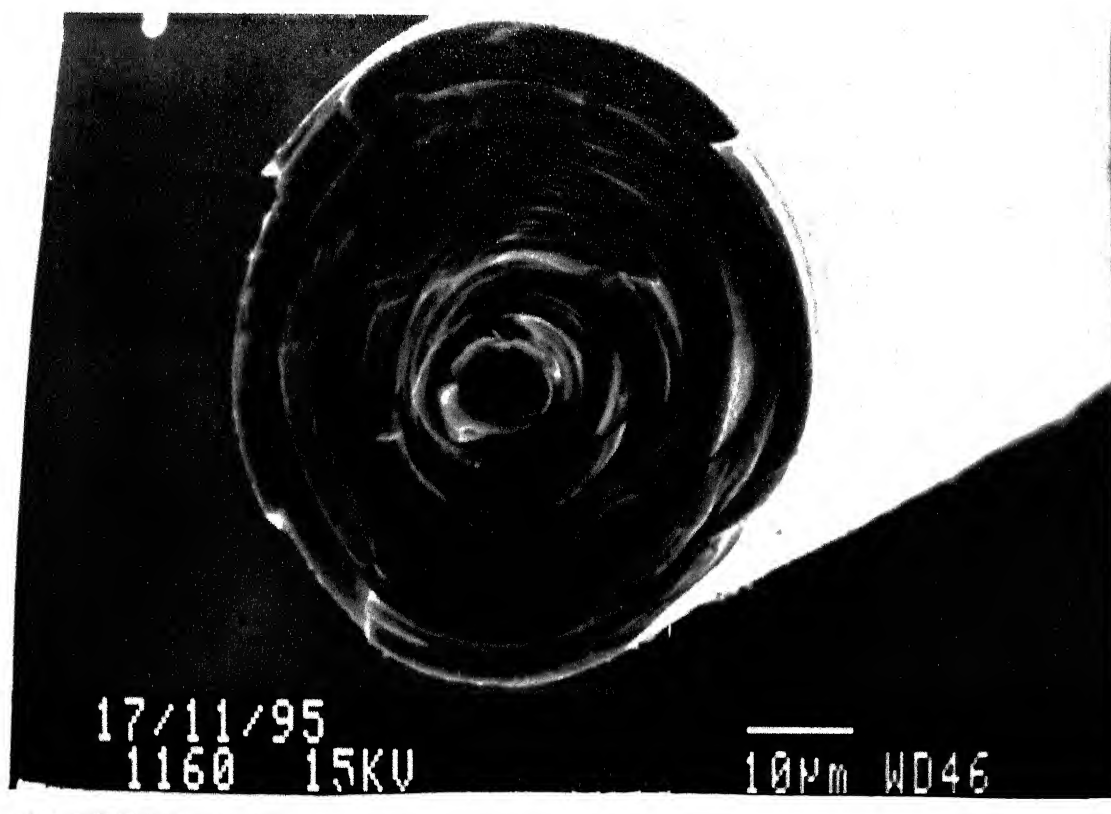


Figure 17 : S.E. Micrograph showing transverse cross-section of fiber.

structure as shown in the Figure 18. At thickening temperature, the fibers are presumably smooth and continuous, but upon cooling the pyrolytic carbon contracts more rapidly in the radial direction than in the circumferential direction. Contraction in the circumferential direction gives the fibers very high compressive hoop stress; the crenulation partially relieves this stress.

For some fibers, especially those formed at high lengthening temperature, there was a noticeable gap between some annular concentric rings (Figure 19) . The reason for this is not clear.

4.5 MECHANICAL PROPERTIES

As mentioned in Section 3.2, stress-strain measurements were made on a Universal Testing Machine and a typical plot of load versus elongation is given in Figure 20. The procedure for calculating the Young's modulus of elasticity and tensile strength from the plot is given in Appendix I.

The variation of Young's modulus (E) with diameter for two different fiber lengths is shown in Figure 21 and 22, where as the corresponding plots for the tensile strengths are shown in Figures 23 and 24. The value of the Young's modulus ranged between 25 -400 GPa. As shown in Figures 21 and 22, the stiffness of these fibers increased with a decrease in diameter. A similar variation of E with diameter has been reported by other investigators. It is well-known that E of VGCF is related to the degree of preferred orientation of the graphite basal planes. The decrease in the stiffness with increasing diameter has been attributed to the diminishing order of the graphite planes(Tibbetts, 1990) . The

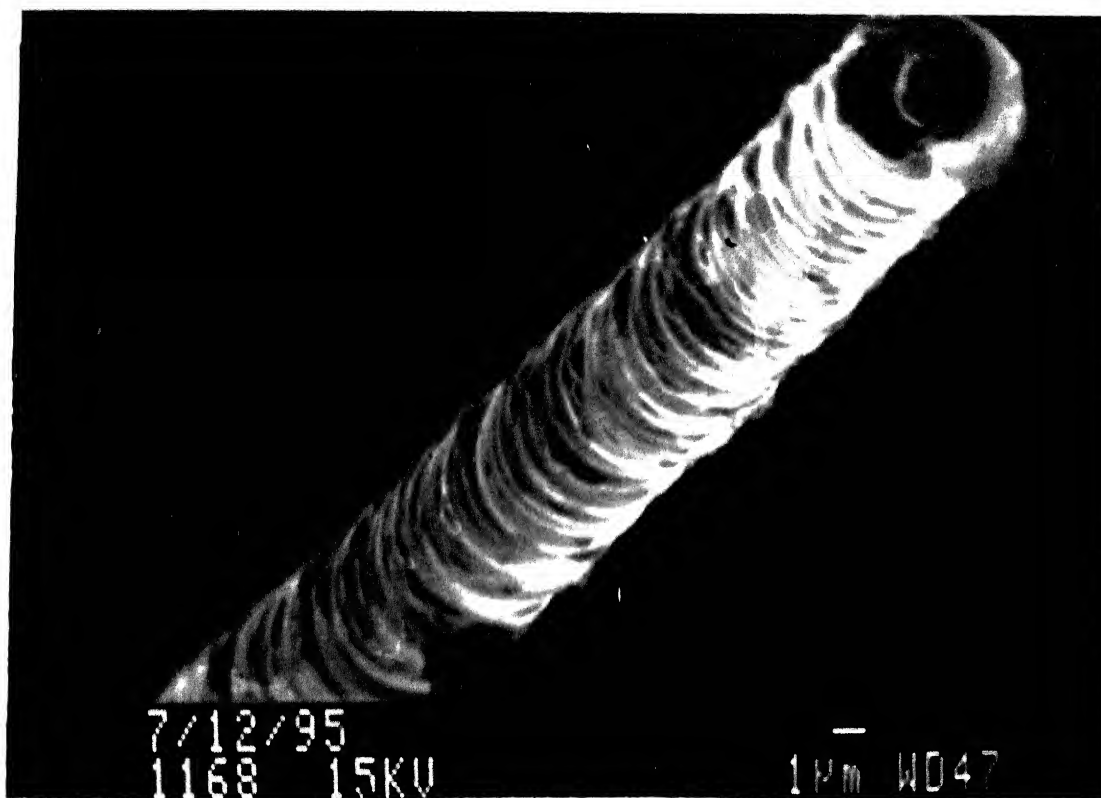


Figure 18 : S.E. Micrograph showing crenulated surface of fiber.

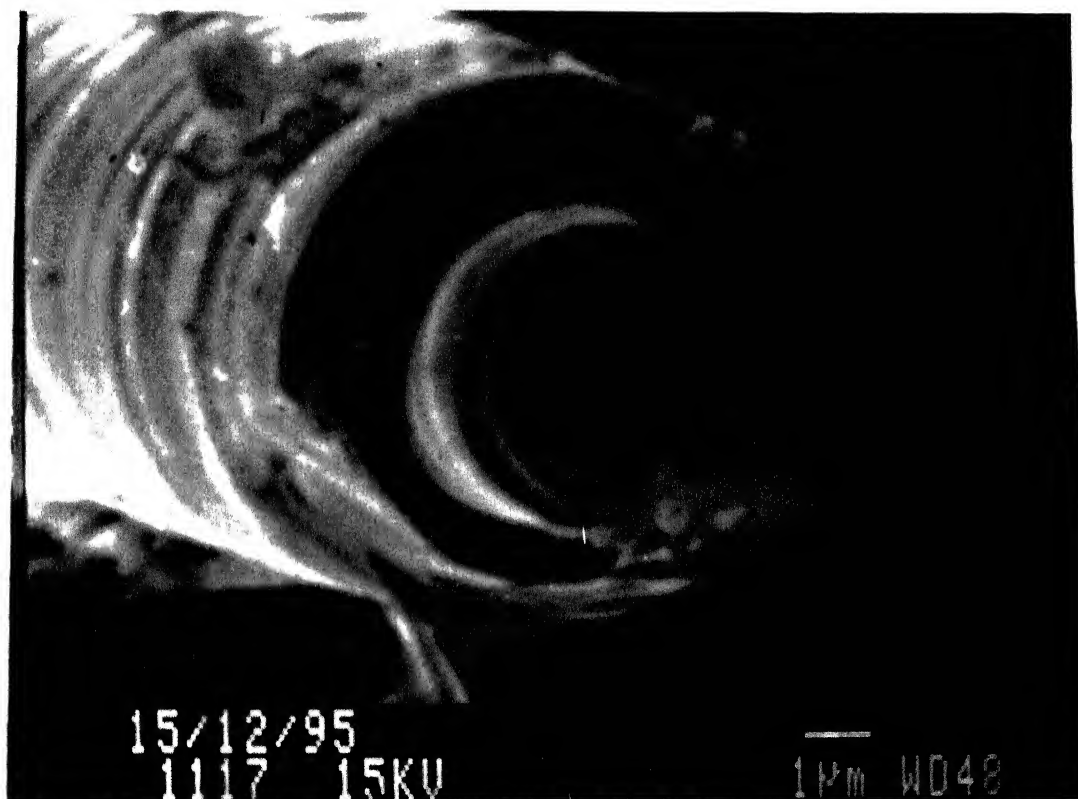


Figure 19 : S.E. Micrograph showing transverse cross-section of high temperature grown fiber.

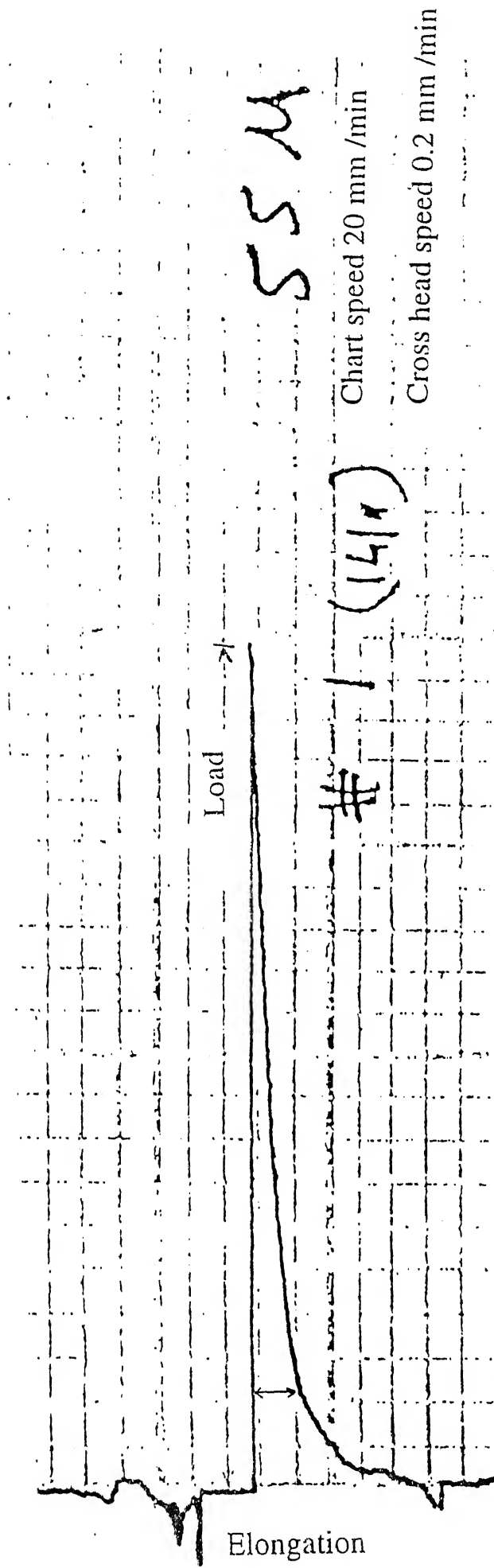


Figure 20 : Load versus Elongation Plot

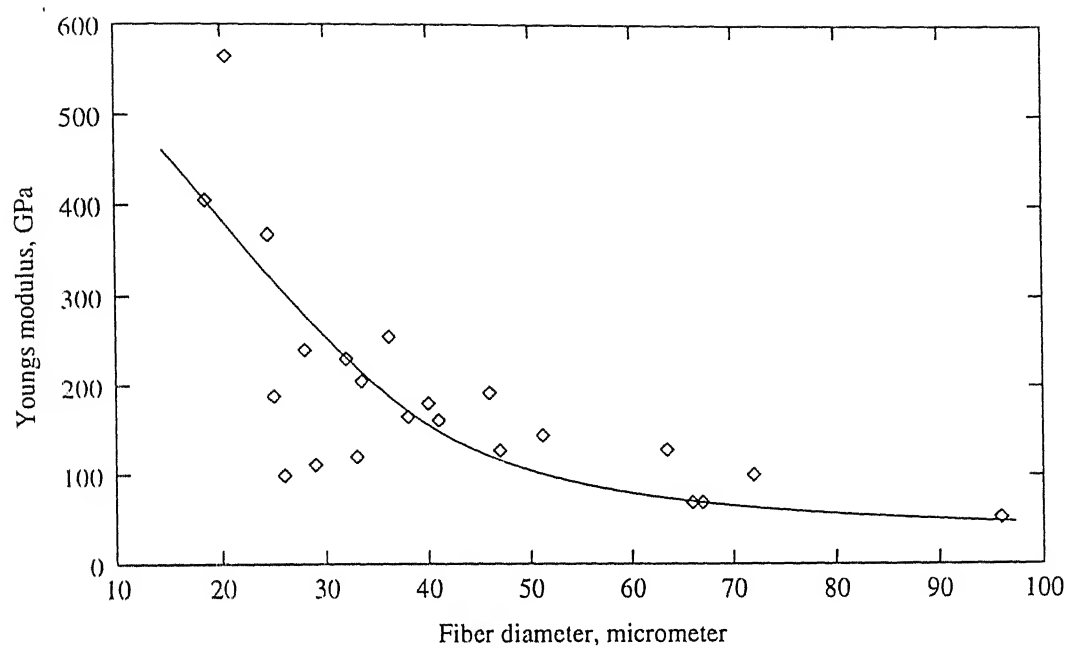


Figure 21 : Variation of Young's modulus with fiber diameter
(Fiber length 15mm.)

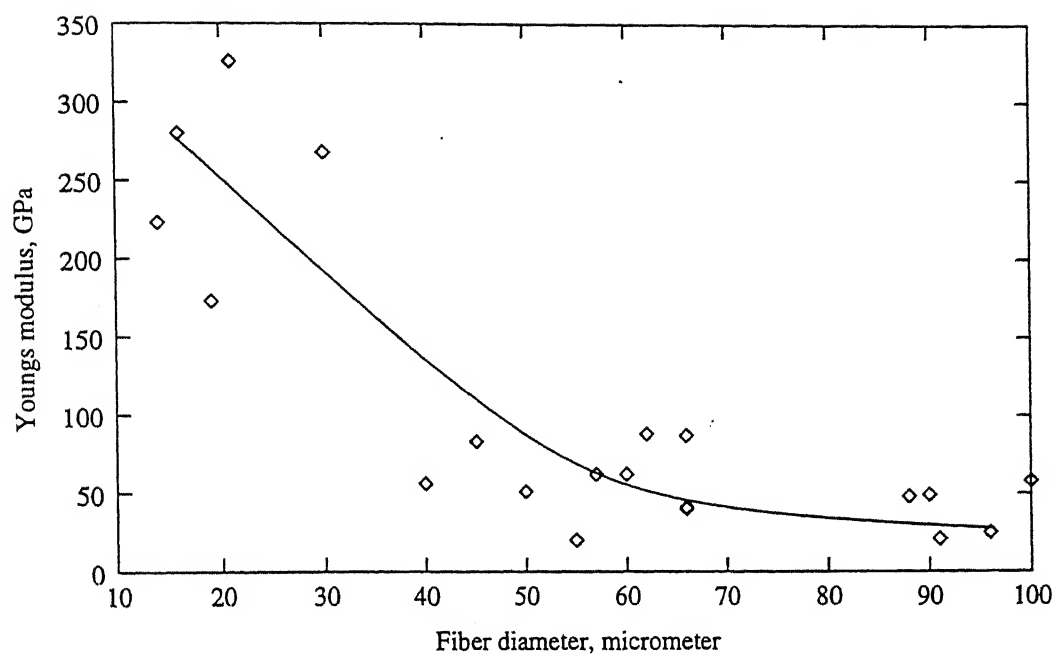


Figure 22 : Variation of Young's modulus with fiber diameter
(Fiber length 10 mm.)

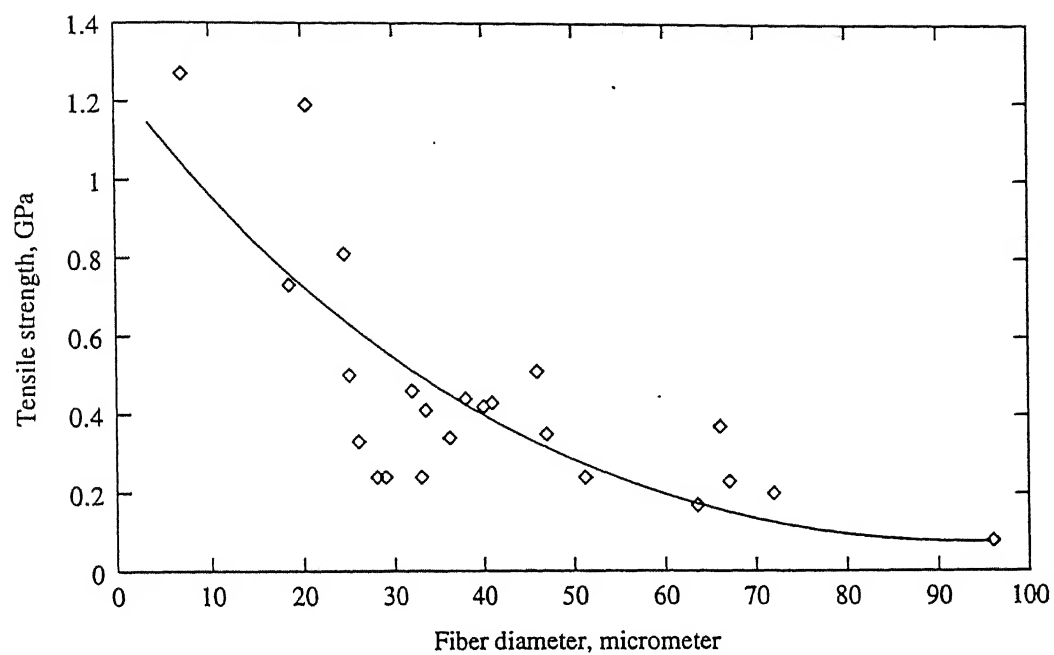


Figure 23 : Variation of tensile strength with fiber diameter
(Fiber length 15 mm.)

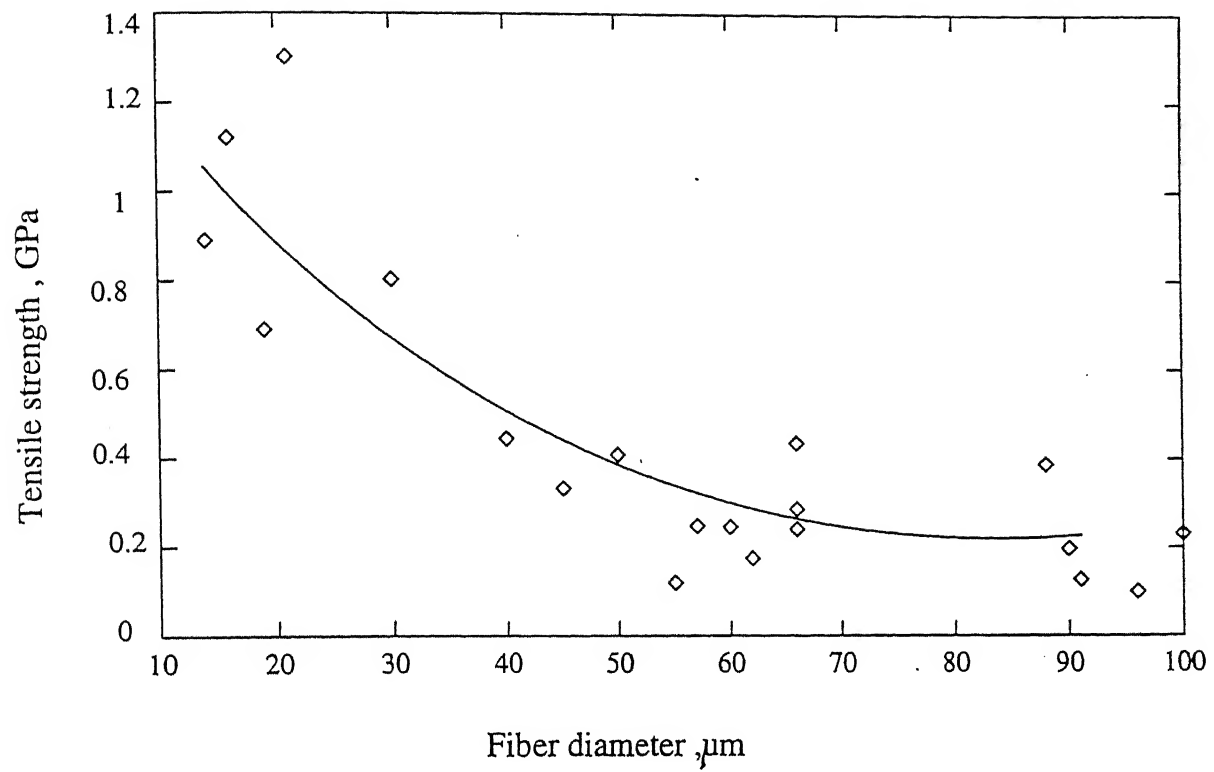


Figure 24 : Variation of tensile strength with fiber idameter
(Fiber length 10 mm,)

reported values of E for VGCF produced from methane vary from 237 GPa for a 7.5 μm diameter fiber to approximately 120 GPa for a fiber diameter of 32 μm (Koyama, 1972) . Ishioka et al. (1992) studied the mechanical properties of VGCF prepared from benzene by the floating catalyst method. The average Young's modulus of straight fibers was 163 ± 33 GPa.

The tensile strength ranged between 0.04-1.50 GPa and decreased with increasing diameter and increasing length. As discussed by Ishioka et al (1992), the tensile strength of the fibers decreases with increasing diameter because of high probability of defects in the thicker fibers. The tensile strength also depends strongly on whether the fiber is straight or crooked. Crooked fibers breaks at a lower tensile force compared to the straight fibers .Similarly, when the fiber is longer, the probability of finding a defect is higher. Thus, the tensile strength is lower for a longer fiber of the same diameter. The adverse effect of increasing the diameter or the length of the fiber on the tensile strength has been explained by Weibull (1951). For benzene derived VGCF , Koyama (1972) reported that the Young's modulus ranged between 179 and 392 GPa and the tensile strength varied from less than 1 GPa for the fiber with diameter of 70 μm to more than 3 GPa for those with diameter less than 5 μm .

Compared to the reported values, the tensile strength obtained in this study is somewhat lower. A reason could be that we have tested fibers of 10 and 15 mm length which is on the higher side. As discussed by Tibbetts (1990) the mean strength of the fibers decreases with increasing length and increasing diameter.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results of this study, the following conclusions can be made:

1. Good yields of carbon fibers can be obtained on alumina substrates in the lengthening temperature range of 1090 to 1150 °C. The average fiber lengths are in the range of 2.8 to 32 mm. The optimum lengthening temperature is in the range of 1120 to 1140, °C.
2. At a constant temperature, the average length of the carbon fiber formed increases with the duration of lengthening and finally reaches an asymptotic value .
3. The deposited carbon fibers have a hollow core and consists of concentric rings of deposited pyrolytic carbon.
4. The diameter of the fibers can be increased by increasing either the inlet benzene partial pressure, gas residence time or the thickening temperature.
5. Depending on the fiber diameter, the tensile strength and Young's modulus vary in the range of 0.1 to 1.4 GPa and 25 to 400 GPa , respectively.
6. The Young's modulus and tensile strength decrease as the fiber diameter increases.

5.2 Recommendations

Following recommendations are proposed for further study :

1. Efforts should be made to measure the catalyst size using TEM.
2. Furnace with a longer heating zone should be used in order to obtain longer fibers in a long tubular reactor.
3. Attempts can be made to study VGCF growth in a floating catalyst reactor.
4. Efforts should be made to grow VGCF using methane as a hydrocarbon source.

We have,

$$\text{Tensile strength} = \frac{\text{Load}}{\text{Cross-sectional area}}$$

or

$$\text{Tensile strength} = \frac{\text{Load} \times 9.8 \times 4}{1000 \times \pi (D^2) \times 10^{-12}}$$

where load is in grams and D (diameter) is in μm .

$$\text{Tensile strength} = \frac{\text{Load}}{D^2} \times 12.48 \quad \text{in GPa}$$

We also have,

$$E \text{ (Youngs modulus) } = \frac{\text{Stress}}{\text{Strain}}$$

Say the chart speed is C mm/min means C/2 div./min on graph paper (1 div.= 2 mm. for the graph paper used) . Also say cross head speed is H mm/min. Therefore, C/2 div/min on the graph is equivalent to H mm/min of fiber elongation.

Therefore the value of one div. is $2 \times H / C$ mm.

or

$$E = \frac{\text{Tensile strength}}{\text{No. of division} \times (2 \times H / C) / L}$$

where L is the length of fiber.

BIBLIOGRAPHY

Aravind, R.; Kunzru , D.and Gupta , S.K. " Vapour Grown Carbon Fibers; Modelling of Filament Length Distributions" J.Anal. and Appl. Pyrolysis, **28**, 255 (1994).

Baker, R.T.K.; Barber, M.A.; Harris, P.S.; Fates, F.S.;and Waite, R.J., " Nucleation and Growth of Carbon Deposits from the Nickel Catalyzed Decomposition of Acetylene " , J. Catalysis **26**, 51 (1972).

Baker , R.T.K. ; Harris , P.S. ; Thomas , P. B. and Waite , R.J " Formation of Filamentous Carbon from Iron, Cobalt and Chromium Catalyzed Decomposition of Acetylene " J.Catalysis , **30** , 86 (1973).

Bansal,P., "Vapor Grown Fiber from Benzene Pyrolysis , Effect of Process Variables" M.Tech.Thesis , Dept. of Chem. Engg., I.I.T., Kanpur (1995).

Bennisad,F.;Gadelle.,P.,Coulon, M. and Bennetain , L." Formation de Fibers de Carbon a Partive du Methane : I Croissance Catalytique et Epaississement Pyrolytique " , Carbon, **26** , 425 (1988a).

Bennisad , F.; Gadelle., P., Coulon, M. and Bennetain , L. " Formation de Fibers de Carbon a Partive du Methane :II Croissance Catalytique et Epaississement Pyrolytique " , Carbon, **26** , 425

(1988b) .

Endo, M. "Grow Carbon Fibers in the Vapor Phase ", Chemtech 18 , 568 (1988) .

Endo, M. and Komaki , " Formation of Vapor Grown Carbon Fibers by Seeding Method of Ultra- Fine Particles ", Extended Abstracts, 16th Biennial Conf. on Carbon, San Diego, ca, p523 (1983) .

Gadelle, P., " The Growth of Vapor Deposited Carbon Fibers", Carbon Fibers Filaments and Composites (Edited by Figueiredo, C.A. Bernardo, C.A. Baker, R.T.K. and Huttinger) , p 95 , Kluwer Dordrecht (1990) .

Galuszka, J. and Back, M. H. Extended Abstract 16 th Biennial Conf. on Carbon San Diego, CA, 21 (1983) .

Gupta, S.K.; Gupta, N. and Kunzru, D., " Vapour Grown Carbon Fibers From the Pyrolysis of Hydrocarbons : Modelling of Filament Growth and Poisoning ", J. Anal. & Appl. Pyrolysis, 26, 131, (1994) .

Hillart, M.; Lang, M., " The Structure of Graphite Filaments ", Zeit Krist, 111, 24 (1958) .

Hou , K. C. ; Palmer , H. B. " The Kinetics of Thermal decomposition of Benzene in a Flow System " J. Phys. Chem., 69 , 863 (1995) .

Hughes ,T.V. and Chambers , C.R., " Manufacture of Carbon Filaments", U.S.Patent 405, 480 (1989).

Ishioka , M.; Okada,T. and Matsubara, K.," Formation of Vapor Grown Fibers in CO -CO₂ -H₂ Mixtures I. Influence on Carrier Gas Composition " Carbon 30, 859 (1992a).

Ishioka,M.; Okada, T.and Matsubara, K.," Formation of Vapor Grown Carbon Fibers in CO- CO₂- H₂ Mixtures , II. Influence on Carrier gas composition ", Carbon , 30, 865,(1992b).

Ishioka, M.; Okada T. and Matsubara, K., " Formation and Characteristics of Vapor Grown Carbon Fibers Prepared in Linz-Donawitz Converter Gas", Carbon,30,,975 (1992c).

Ishioka, M.; Okada T. and Matsubara , K. , " Preparation of Vapor Grown Carbon Fibers in Straight Form by Floating Catalyst Method in Linz- Donawitz Converter Gas",Carbon, 31, 123, (1993).

Jayasanker,M.; Kunzru,D.;Gupta S.K. and Chand, R.,"Vapour Grown Carbon Fiber from Benzene Pyrolysis", Carbon, 33, 253, 1994.

Jayasanker, M., " Vapour Grown Carbon Fiber from Benzene Pyrolysis ", M.Tech Thesis, Dept. of Chem.Engg., I.I.T.,Kanpur (1994).

Jayasanker, M., Agarwal, N., Chand, R., Gupta, S.K. and Kunzru, D., "Vapor Grown Carbon Fibers from Benzene Pyrolysis Filament Length Distribution " Carbon ,1996 (in press)

Kato, T.; Haruta, K.; Egashira, M. and Kawasumi, S., " Formation of Carbon Fibers from Naphthalene on Some Sulfur Containing Substrates" Carbon , 19,148, (1981).

Kato, T.; Haruta, K.; Haruta, K.; Kusankabe , K. and Morooka, S . " Formation of Vapor-Grown Carbon Fibers on a Substrates" Carbon 30, 989 (1992).

Katsuki, H. ; Koji, M.; Makota, E. and Kawasumi , S. " Formation of Carbon Fibers from Naphthalene on Some Sulfur Containing Substrates" Carbon 19, 148, 1981.

Koyama, T., " Formation of Carbon Fibers from Benzene", Carbon, 10, 757 (1972).

Koyama , T.; Endo, M. and Onuma, Y., " Carbon Fiber Obtained by Thermal Decomposition of Vaporized Hydrocarbon" Jap. J. Appl. Phy., 11, 445, (1972).

Lacava, A.I.; Raone, D.F.E. and Caraballo, " Effect of Hydrogen on the Iron and Nickel Catalyzed Formation of Carbon From Benzene" ACS Sym. Ser., 202, 82 (1982).

Madranero, A. " Possibility for the Vapor Grown Carbon Fiber

Growth Process " J.Mater.Sc. **30** , 2061, (1995) Eng..

McAllister , P. ; Hendricks , J. F. and Wolf , E. E. " The Infiltration of Carbon Fiber Felts and Composites by Pyrolytic Carbon Deposition from Propylene" Carbon, **28** , 579, 1990.

Oberlin,A.;Endo,M.and Koyama, T.," Filamentous Growth of Carbon Through Benzene Decomposition", J. Cryst.Growth, **32**,335(1976) .

Tibbetts,G.G., " Carbon Fibers Produced from the Pyrolysis of Natural Gas In Stainless Steel Tubes " Appl. Phy. Letters ,**42**, 666 (1983) .

Tibbetts , G.G. , " Length of Carbon Fibers Grown from Iron Catalyst Particle in Natural Gas " , J. Cryst. Growth, **73**,431 (1985) .

Tibbetts,G.G.,Devour,M.G.," Regulation of Pyrolysis Methane Concentration in the Manufacture of Graphite Fibers ", U.S.Patent 4565, **684** (1986) .

Tibbetts, G.G., Devour, M.G. and Rodda , E.J., " An Adsorption Isotherm and its Application to the Growth of Carbon Filaments on Iron Catalyzed Particles " Carbon , **25**, 367, (1987) .

Tibbetts,G.G. and Beetz, Jr., C.P. " Mechanical Properties of Vapor-Grown Carbon Fibers ", J.Phys D: Appl.Phys. **20**, 292,(1987) .

Tibbetts,G.G.;Rodda, E.J.," High Temperature Limit from the Growth of Carbon Filaments on Catalytic Iron Particles ", Mat.Res.Soc.Sym.Proc., 11, 49, (1988).

Tibbetts,G.G.,"Vapor Grown Carbon Fibers " , Carbon Fibers Filaments And Composites , Editors , J.L.; Figueiredo , C.A. ;Bernardo;R.T.K.Baker and K.J.Huttinger , p73, Kluwer Academic Publisher, Netherland (1990).

Tibbetts, G.G. " Growing Carbon Fibers with a Linearly Increasing Temperature Sweep : Experiments and Modeling ", Carbon, 10,309, (1992).

Tibbetts, G.G.and Garkiewics, W.D. , " A New Reactor for Growing Carbon Fibers from Liquid and Vapor-Phase Hydrocarbon" Carbon , 31, 809 (1993).

Tibbetts,G.G.;Bernardo,C.A.; Gorkiewicz, W.," Role of Sulfur in the Production of Carbon Fibers in the Vapor Phase", Carbon, 32,569, (1994).

Weibull,W.(1951)" A Statistical Distribution Function of Wide Applicability" J.Appl.Mech. 18,293,1951.